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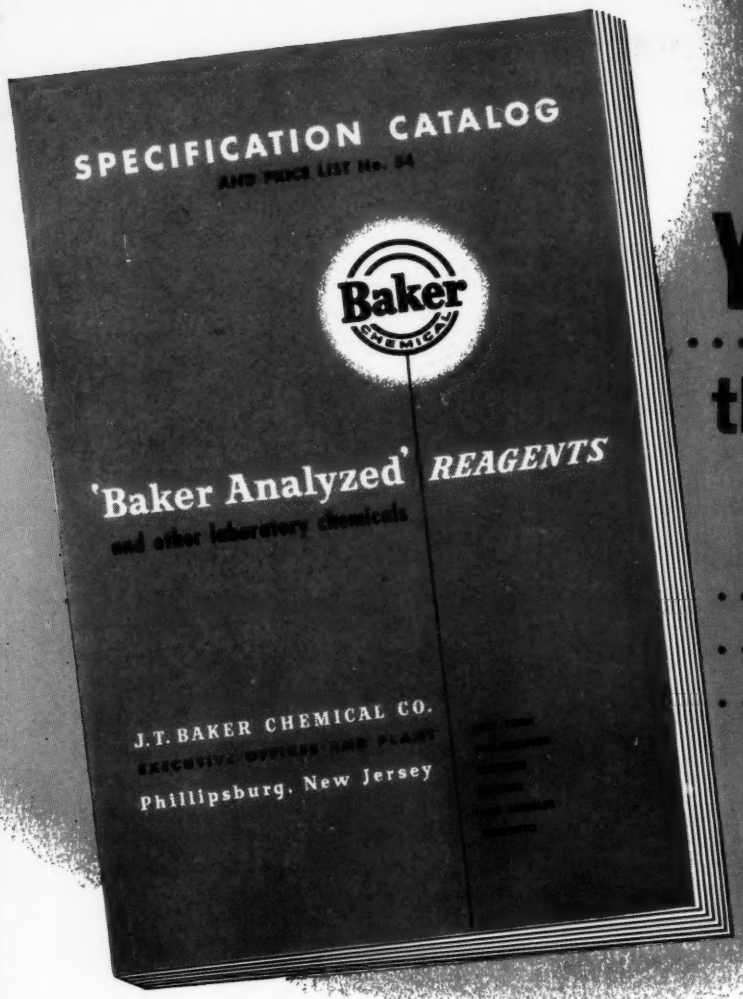

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VOLUME 31

August, 1954

NUMBER 8

JOURNAL OF CHEMICAL EDUCATION

Photometric Titrations, *Arthur L. Underwood* 394
Haus Energie, *Ralph E. Oesper* 398
The Origin of Petroleum, *T. W. Nelson* 399
The Liebig-Pasteur Controversy, *Harold Finegold* 403
Contributions of Liberal-arts Colleges to the Journal of Chemical Education, 1934–53, *John R. Sampey* 406
The Platinum-group Metals, *John Cochrane* 407
The Variation of Equivalent Conductance with Concentration, *John T. Stock* 410
Lavoisier's Proposals for French Education, *Harold J. Abrahams* 413
A Kinetic Interpretation of the Bouguer-Beer Law, *J. H. Goldstein and R. A. Day, Jr.* 417
Experiments Most Often Required in College General Chemistry, *Dorothy S. Lewis* 418
Clara Marie DeMilt (1891–1953), *John Mark Scott* 419
Sublimation Curve, Vaporization Curve, and Triple Point Determination, *Norman O. Smith and Constance M. Costich* 421
Partition Chromatography, an Isentropic Separation Process, *A. Klinkenberg* ... 423
Some Trends in the Teaching of General Chemistry, *Carl R. Meloy* 424
The Brönsted Theory Applied to Acid-Base Balance and Respiration, *Arthur W. Devor* 425
Proper Place Problems, *Scott MacKenzie* 428
The Examination Question, *F. E. Condon* 430
A Kinetic Analogy, *Robert Lemlich* 431
The Quantitative Analysis Notebook, *C. Kinney Hancock* 433
"What I Find Hardest to Believe," *Samuel Weiner* 434
Proceedings of the Pacific Southwest Association of Chemistry Teachers Meeting of the Northern Section 436
Report of the New England Association of Chemistry Teachers Official Business 437
Division of Chemical Education of the American Chemical Society 440

Editor's Outlook 393
Out of the Editor's Basket 21
Advertisers' Index 32
Recent Books 441
Frontispiece—Clara Marie DeMilt (1891–1953) 17

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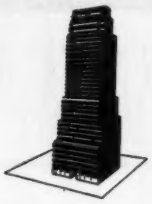

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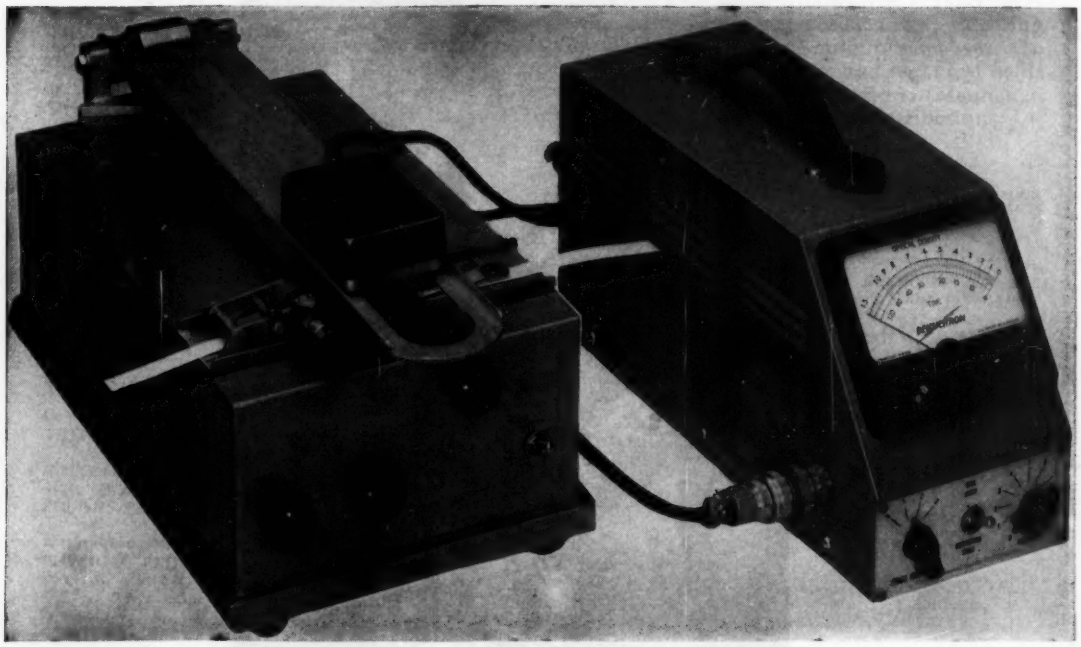

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Editor's Outlook

LAST month I asked the question, "What makes a good teacher?" Let us now consider: "How can we make a good teacher?" On this point, Dean Elmer Ellis of the University of Missouri makes some remarks in a recent article[1] which will be worth elaborating.

He picks up the discussion at the point we left it, after considering the common criticism of the graduate school for its failure to train college teachers adequately. He accepts this as inevitable—that is, to the extent that exclusive emphasis upon subject matter implies inadequate training. He points out that this subject-matter emphasis is the primary objective of the graduate school, for which it exists and which it cannot avoid, and from which it cannot risk being diverted by any other objective. Subject-matter preparation is the one aspect of the future college teacher's education which only the graduate school can give. Otherwise, adequate preparation becomes entirely a matter of later self-education.

The undergraduate department in which the young teacher later finds himself can do little about this; nevertheless, it *can* do something about his introduction to teaching, by providing an on-the-job training which can go a long way toward meeting the need. No college, thinks Dean Ellis, needs to accept poor teaching as inevitable unless it wants to. The opportunity and the facilities for avoiding it are at hand; it is only necessary to set up a little machinery.

Other agencies—such as industry and the independent research institutions—compete with the colleges for the product of the graduate schools, and usually with conspicuous success. But these agencies do not assume that the newly-fledged Ph.D. is a finished scholar; they usually put him through some sort of in-service training program before giving him any great responsibility. Why should the college do less?

The nature of such a training program and the manner of its organization must depend upon the particular local circumstances, but there are certain obvious and desirable features. The new instructor must not be given too heavy a teaching load, nor a motley array of different courses which requires elaborate and painful preparation on his part. He should be required to visit courses similar to his own, conducted by competent and successful teachers who in turn visit *his* classes and are then available for consultation and advice. A seminar or discussion group of some kind should be organized, including all new instructors in the department or in the whole college, at which their various teaching problems are dealt with, by themselves and by others who are competent and able to contribute experience.

"Most important of all," says Dean Ellis, "an atmosphere of approval for good teaching must prevail. Prestige for superior teaching must be present in all places in the college, including the student body and the administration."

This solution to the problem of college teacher-training has at least one virtue: It puts the responsibility where it may seem to be most appropriate. It is perhaps the *only* plausible solution if one is disposed to accept the original assumption that the graduate school cannot and should not take the responsibility for it. It must be admitted that college administrations are as likely to shirk the responsibility as others have been, but it may be replied that in such case they should not thereafter make any complaint. However, the complaint about the present situation does not come entirely from college administrations, but also from students, the public, and from teachers themselves.

Should this solution be adopted it would of course not be universal. There would be many places where the situation remained hit-or-miss. The young prospective college teacher would then have to be more than ever critical in accepting his first appointment, to be sure that it offered him the training opportunities which would start him off on a successful career in his chosen profession. Perhaps this might be a very desirable outcome.

[1] ELLIS, E., "Making competent teachers of new instructors," *J. Higher Educ.*, 25, 204 (1954).

PHOTOMETRIC TITRATIONS

ARTHUR L. UNDERWOOD
Emory University, Emory University, Georgia

THE literature contains relatively few references to the technique of photometric titration, although both the theory and the instrumentation necessary for its wider application have been available for a number of years. Methods which seem far more troublesome are much more widely used. On the assumption that this status does not reflect fairly the utility of photometric titrations, this paper will call attention to the method, and discuss briefly some previous applications and some possibilities for future work.

As an introduction, consider titrimetric methods in general. Briefly, one desires to ascertain the point at which just enough reagent has been added to represent chemical equivalence to a substance in solution in a well characterized reaction, by observing some property of the solution. In order for this "stoichiometric" or "equivalence" point to be found accurately, the equilibrium in the reaction must lie far toward completion, so that the equivalence point will be attended by a large and sudden change in the concentration of one of the reactants. When this change has proceeded sufficiently to activate our means of observation, we secure an "end point." Chemical indicators which respond with a color change to dramatic changes in the hydrogen ion concentration, or the oxidation potential, of a solution are, of course, well known. The limitations of such visual indicators are likewise well known. Thus numerous "instrumental" titrations have been developed, some of which are widely used. Potentiometric, amperometric, conductometric, and thermometric titrations serve as examples of these. In some cases, such methods enable us to locate end points in solutions where chemical indicators would be obscured, *e. g.*, highly colored solutions. In other cases, indicators are unavailable. But, in addition, the instrumental methods are attractive in extending the advantages of titrimetric analysis to titrations which are inherently nonfeasible by "classical" indicator methods because of equilibrium conditions in the reactions. In other words, an instrumental end point need not be "sharp" to be useful.

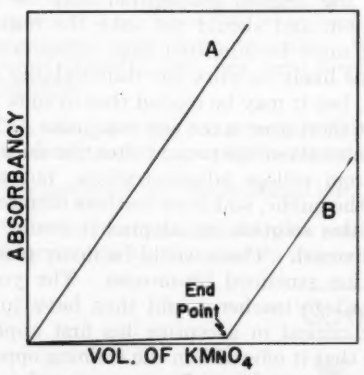

Figure 1. Photometric Titration

Curve *A:* addition of $KMnO_4$ to water. Curve *B:* titration of reducing agent.

Various properties of solutions may be "followed" to assess the progress of titrations. The absorbancy (log I_0/I: variously designated extinction, optical density, etc.) of a solution may be invoked for this purpose. Consider a large beaker of water into which we add, from a buret, successive portions of a potassium permanganate solution. Let the permanganate solution be sufficiently concentrated for the volume change during the addition to be negligible. If we measure the absorbancy of the solution after adding each increment of permanganate (at a wave length where permanganate absorbs appreciably), and plot these values against the volume of permanganate, we obtain an ordinary Beer's law curve for permanganate, as shown in Figure 1. Now suppose we repeat the titration, adding permanganate not to a beaker of water but to a solution of a reducing agent such as a ferrous salt. Since the permanganate color is destroyed so long as ferrous ion remains, our Beer's law plot for permanganate will be delayed until the reducing agent has been exhausted. This situation is also shown in Figure 1. Simple as it may be, this example illustrates what is meant by a photometric titration.

ADVANTAGES OF PHOTOMETRIC TITRATIONS

Availability of Apparatus. The experimental setup for performing photometric titrations is easily achieved by very simple adaptations of existing photometric instruments. Such work could probably be done with any photometer, although a good spectrophotometer having a stable electrical circuit and furnishing a wide wave-length choice is, of course, preferable. Goddu and Hume (*1*) have devised a very simple and inexpensive adaptation for the Coleman Model 14 spectrophotometer. Bricker and Sweetser (*2*) have employed the Beckman Model DU spectrophotometer with a similarly simple modification. The Beckman Model B instrument is likewise readily adapted. We have found the test tube attachment supplied by the manufacturer for use with the Beckman Model DU to serve admirably. The titration cell, similar to that of Goddu and Hume (*1*), consists of a 150-ml. beaker with a section of Pyrex tubing sealed into the bottom. This

tube fits into the bracket intended for test tubes, where it is held quite securely. The cover for the test tube attachment encloses the entire cell. Two holes are drilled in the cover to admit stirrer and buret; if these are protected by felt gaskets, and the stirrer and buret are painted black at the point where they enter, the assemblage is perfectly light-tight. Only a few minutes are required to assemble this adaptation or to restore the instrument for conventional use. The stability of the Beckman instrument, and its excellent optical system make it very attractive for photometric titrations.

Relation of Absorbancy to Concentration. Photometric titrations share with the amperometric and conductometric techniques an important advantage in that the measured property (absorbancy) is directly proportional to the concentration of the substance being "followed." This fact is apparent from the familiar Bouguer-Beer expression: $A_s = a_s bc$, where A_s represents absorbancy, a_s is the so-called absorbancy index, b the length of the light path through the solution, and c the concentration of the absorbing species. This direct relationship is to be contrasted with that pertaining to a potentiometric titration. In this case, the measured property (the potential of an indicator electrode) is related not directly but logarithmically to the concentration of the substance involved, as expressed in the familiar Nernst equation. Thus reasonably good photometric end points may be expected in certain cases where potentiometric end points have become indistinct.

Accuracy. The accuracy to be expected in a photometric titration may be compared with that attainable in ordinary photometric analysis: in the latter case, one measurement of absorbancy is converted into the analytical result, whereas the photometric end point, as with amperometric or conductometric end points, is generally given by the intersection of two straight lines whose slopes are determined by a number of points. This same principle applies in comparing, say, amperometric titrations with isolated measurements of diffusion currents.

Reasonable extrapolation is permissible in cases where the lines deviate from linearity in the vicinity of the end point, since absorbancy values in this region of the curve are no more significant than values far on either side of the end point. Thus the photometric technique permits the extension of titrimetric analysis with reasonable accuracy to certain reactions which are incomplete at the equivalence point. It shares this advantage with some of the other instrumental methods, of course.

Versatility. As discussed in the section on applications, photometric titrations may be performed on a wide variety of systems. Acid-base, oxidation-reduction, precipitation, and complex-forming reactions have all been found amenable to the technique. Furthermore, photometric titrations should prove extremely useful for studies in nonaqueous media, where it is frequently difficult to find suitable indicator electrodes for potentiometric work. By employing an instrument with which the ultraviolet region of the spectrum is accessible, vast possibilities are opened up for photometric titrations.

APPLICATIONS

Acid-Base Titrations. This field has been thoroughly explored by Goddu and Hume (*3*). The photometric method grants great precision to determination of the end point in conventional acid-base titrations with colored indicators. Furthermore, with organic acids or bases which are colored (or which absorb in the ultraviolet) indicators can be dispensed with, along with the attendant indicator errors. Solutions of acids can be titrated satisfactorily if the product of concentration and ionization constant equals or exceeds 10^{-12}.

Oxidation-Reduction Titrations. Several examples of photometric end points in oxidation-reduction titrations have been presented. Goddu and Hume (*1*) found that the ferrous sulfate-persulfate method for the determination of vanadium in steel was improved when the permanganate titration of vanadyl ion was followed spectrophotometrically. The first use of the ultraviolet region of the spectrum, employing the Beckman Model DU instrument, was described by Bricker and Sweetser (*2*). Ceric ions exhibit a strong absorption band at 320 mμ, whereas cerous, arsenious, and arsenic ions do not absorb at this wave length. Thus it was possible to titrate arsenious solutions with ceric sulfate, using a photometric end point. Microgram quantities of arsenic could be titrated with very dilute ceric solutions, with errors as small as one or two parts per thousand.

Sweetser and Bricker (*4*) showed that photometric end points could be applied profitably to volumetric oxidations with bromate-bromide solutions. The absorption of the tribromide ion in the ultraviolet was used in detecting the end points. By varying the wave length, titrations could be performed with bromate solutions of varying normalities. Trivalent arsenic and antimony were successfully titrated in this way. Furthermore, the method was applicable to titrations involving bromine addition and substitution reactions with organic compounds. Bromine addition titrations of cholesteryl acetate, oleic acid, and several other unsaturated compounds were described. Phenol, aniline, *o*-cresol, and several other compounds capable of undergoing substitution reactions with bromine were likewise determined in this way. The advantages of the photometric end point in bromate-bromide titrations were pointed out (*4*). Notable among these is the fact that excess brominating agent can be added, forcing to completion bromination reactions that are slow in the vicinity of the end point. The end point is then obtained by extrapolation rather than back-titration.

Recently Bricker and Sweetser (*5*) developed a photometric titration in which uranium and iron could be determined simultaneously by oxidation with ceric sulfate. The potentials of the uranyl and ferrous systems differ sufficiently to give two consecutive end

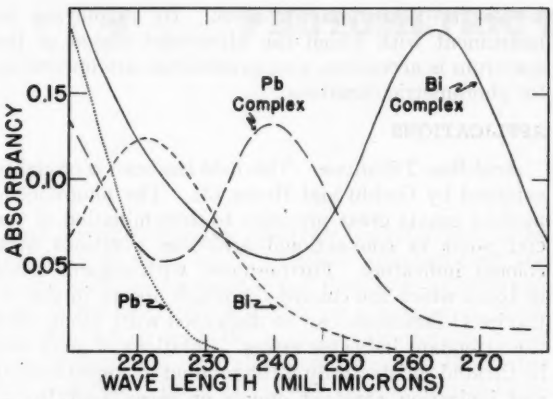

Figure 2. Absorption Spectra of Bismuth and Lead and Their Complexes with Ethylenediaminetetraacetic Acid

2×10^{-4} *M* Pb^{++} and Bi^{+3} in 0.01 *M* $HClO_4$ (complexes at same concentration).

points when a mixture of the two is titrated with a ceric solution. With the spectrophotometer set at a wave length where ferric ion absorbs considerably, the titration is commenced. A sudden rise in the titration curve, indicating the formation of ferric ion from ferrous, shows the end point in the uranyl titration, since uranyl ions react first with the ceric solution. The wave length is then shifted to a value where ceric ion absorbs strongly, and the titration is continued. A sudden rise in the curve, indicating the presence of excess ceric ion, shows that the ferrous ion has reacted completely. Milligram quantities of uranium and iron can be determined with errors less than ten parts per thousand.

Turbidimetric Titrations. Phototurbidimetric titrations based on the precipitation of barium sulfate have been described by several workers (*6*, *7*, *8*). Maximum turbidity readings were found to correspond to the equivalence points provided conditions were very carefully regulated. The concentration of the sample must be high enough for one drop of precipitant to cause immediate precipitation, but low enough for the precipitate to remain suspended. Addition of miscible organic solvents, and protective colloids such as gum arabic, are helpful. Nichols and Kindt (*8*) also described a photometric titration method for studying the critical concentration for the formation of micelles in soap solutions. The method is based on the fact that alterations in the absorption spectra of certain dyes reflect the formation of oriented soap aggregates.

Under the designation "heterometric titrations," Bobtelsky and his co-workers have employed turbidimetric measurements in a number of titrations. Among the reactions investigated were the precipitation of ferric, chromic, and aluminum phthalates from aqueous ethanol (*9*), precipitation of nickel with dimethylglyoxime (*10*), and the precipitation of lead with citrate (*11*). As tends to be true of turbidimetry in general, photometric titrations based on turbidity measurements are naturally somewhat limited in applicability, although excellent results are obtained in certain cases.

Titrations Involving Complex Formation. In this field good indicators are at a premium, and photometric titrations as well as other instrumental methods are most attractive. In one of the first studies, Nichols and Kindt (*8*) applied a photometric end point to the well known Willard and Winter titration of fluoride with thorium nitrate. When the dye alizarin red S is used as indicator, the end point in the fluoride titration is attended by conversion of the dye from its free form to the complex with thorium. The resulting color change is rather indistinct, and the titration is generally held to have a "difficult" end point. The photometric end point was quite satisfactory, although turbidity owing to the precipitated thorium fluoride was troublesome.

The chelating agent ethylenediaminetetraacetic acid (Versene, Sequestrene, etc.) is known to form extremely stable complexes with a number of metal ions (*12*). Because of the polydentate nature of this reagent, the complexes formed under ordinary conditions are 1:1 complexes, *i. e.*, one mole of chelating agent combines with one mole of cation. This fact circumvents one of the primary difficulties in using complexing agents as titrants for metal ions, *viz.*, the stepwise formation of successive complexes to satisfy the coordination requirements of the metal, resulting in a "smearing-out" of the end point in a titration. But one of the principal deterrents to the application of ethylenediaminetetraacetic acid as a titrimetric reagent has been the lack of suitable indicators. In a few cases, satisfactory indicators are available, as in the well known water hardness titration. But this problem has hampered the development of titrimetric methods for metal ions.

Sweetser and Bricker (*13*) were the first to perform photometric titrations with ethylenediaminetetraacetic acid. They showed that copper ion could be titrated to a sharp end point by working at a wave length where the copper complex with the titrant absorbs more strongly than copper-aquo complex. A deepening of the blue copper color attends the formation of the complex with the titrant. The end point would be sufficiently sharp for visual work but for the fact that one cannot titrate until a solution stops becoming more blue. Nickel ion was titrated in the same fashion. The titration of ferric iron was based on the fact that the ferric complex with salicylic acid was broken down in favor of the colorless ethylenediaminetetraacetic acid complex. The disappearance of the red ferric salicylate color was followed spectrophotometrically.

The stability constants of the complexes formed by many metal ions with ethylenediaminetetraacetic acid have been measured. Inspection of these constants suggests the possibility of determining more than one metal ion in a single titration, *i. e.*, some of the constants differ sufficiently to give consecutive end points in titrating certain mixtures. The first example of such a titration has been reported (*14*). In this case, iron and copper are determined in a single titration. The

ferric complex is much more stable than the cupric complex; thus, when ethylenediaminetetraacetic acid is added to a mixture of iron and copper, the iron reacts first. With a spectrophotometer set at a wave length where the cupric complex absorbs but the ferric complex does not, there is no increase in absorbancy until the iron has been titrated, after which there is a steady increase, followed by a plateau representing complete reaction of the copper.

Bismuth, which forms a very stable complex with ethylenediaminetetraacetic acid, may be titrated by following spectrophotometrically the disappearance of the yellow bismuth-thiourea complex. Alternatively, as was true with iron, the end point in the bismuth titration may be located by the abrupt formation of the copper complex with the titrant. Bismuth and copper may both be determined in a single photometric titration, of course (*15*).

Titrations with ethylenediaminetetraacetic acid in the visible region of the spectrum are limited to those cases where suitable colored indicators may be found or where the metal ion itself is colored; complex formation with this reagent does not confer color upon otherwise colorless ions. In many cases, interfering ions exert their influence by interacting with the indicators rather than by participating in the reaction with the titrant (*16*). The reagent itself absorbs in the ultraviolet, however, as do many of its metal complexes, and indeed, many metal ions. For example, bismuth and lead exhibit ultraviolet absorption bands, the position and intensity of which depend somewhat on the nature of the anions in the solutions. The complexes of these metals with ethylenediaminetetraacetic acid also absorb very strongly. The spectra are shown in Figure 2. By choosing suitable wave lengths it has been possible to titrate lead and bismuth solutions as dilute as 10^{-6} *M* with exceptionally good end points. Furthermore, end points for both bismuth and lead may be obtained in a single titration of the mixture because of

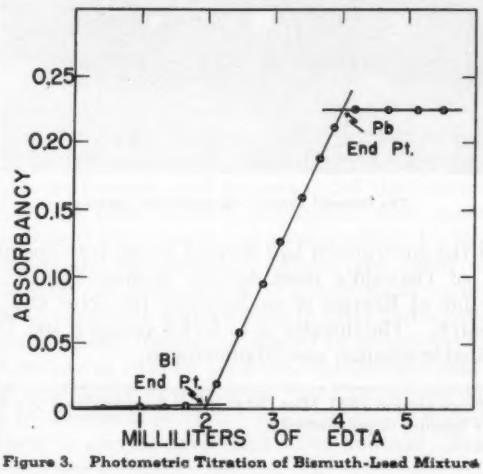

Figure 3. Photometric Titration of Bismuth-Lead Mixture

0.21 mg. Bi and 0.21 mg. Pb titrated with 5×10^{-4} *M* ethylenediaminetetraacetate. Volume; 100 ml.; λ:235 mμ.

fortunate relationships between bismuth and lead with regard to both stability constants of the complexes and to their absorption spectra (*17*). A typical titration curve is given in Figure 3. It seems clear that thus far only a few of the possibilities of photometric titrations with chelating agents have been exploited.

Fundamental Information. In addition to the analytical applications already pointed out, there are a few examples of photometric titrations which were performed solely to obtain information regarding reaction stoichiometry or other fundamental data. In one of these, Yoe and Jones (*18*) employed the technique to study the composition of iron complexes with the reagent Tiron (disodium-1,2-dihydroxybenzene-3,5-disulfonate). Tarbell and Bunnett (*19*) used photometric titrations to elucidate the composition of the products formed in the reaction of di-(*p*-biphenyl)-thiocarbazone with certain arsenicals. In a recent study of relative acid strengths of certain Brönsted acids, Kolthoff, *et al.* (*20*), carried out photometric titrations of iodine monochloride with pyridine in chloroform and in nitrobenzene solutions.

No attempt has been made in this paper to present an exhaustive bibliography. We have merely endeavored to call attention to photometric titrations as an important and useful tool, giving sufficient examples to orient the reader. It is believed that the method will eventually attain a significant status in modern analytical chemistry.

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HAUS ENERGIE

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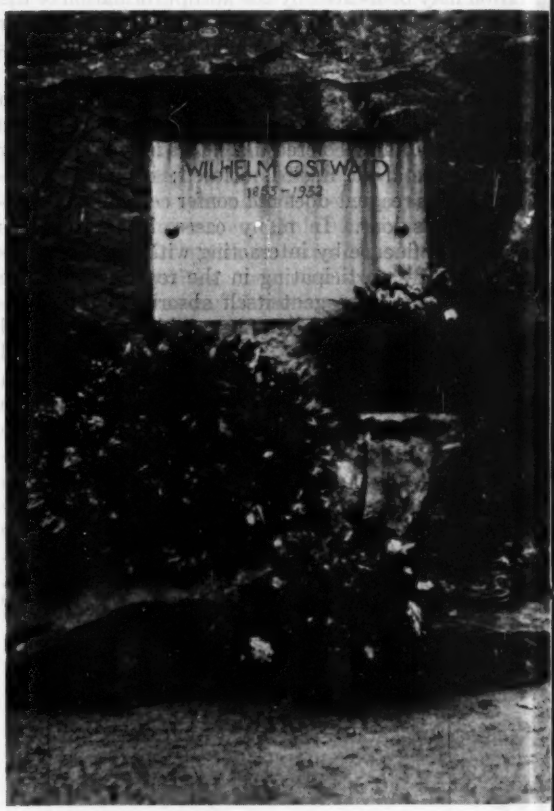
Haus Energie

In 1901 Wilhelm Ostwald bought a large tract of land together with its run-down house at Grossbothen, then about one hour by train from Leipsic. When, in 1906, he resigned his chair at the University of Leipsic, he moved his family and his tremendous library to this peaceful country home. The old house was remodeled and a commodious laboratory installed. The estate was renamed "Energie" and the dwelling became "Haus Energie." Here he continued his manifold activities until his death on April 4, 1932.[1] His ashes, together with those of his wife (1854–1946), rest in a catacomb sculptured out of the living rock on the estate.

Haus Energie now houses the wonderful collection of books, periodicals, unpublished manuscripts, etc., which made up his literary estate. It has been organized into the Wilhelm Ostwald Archiv and is administered by his daughter Grete and his son-in-law Eberhard Brauer. They are striving not only to preserve this intellectual treasure but to make effective use of it.

The centenary of Ostwald's birth came on September 2, 1953. Miss Ostwald honored the occasion by issuing a 320-page biography, "Wilhelm Ostwald, mein Vater," a remarkably fine record of this great life, composed essentially from the personal and human side.

The University of Leipsic celebrated the occasion by suitable ceremonies, including eulogies and appropriate music. The program was high-lighted by the arrival on the stage of an emissary from the civil authorities (Saxony is now Soviet territory) who announced that the Academy of Sciences would henceforth enter into possession of the whole Ostwald estate and take under its special protection not only the Archiv but also its directress.[2] To the delight of all, it was also announced



The Ostwald Crypt at Grossbothen, Saxony

that the government had decided to put into operation one of Ostwald's most fervent wishes, namely the erection at Energie of an Institute for color and dye research. The director is to be his youngest son, Otto, a capable scientist and administrator.

[1] The autopsy showed complete exhaustion of some of the organs. The brain was uncommonly large and very highly convoluted.

[2] Since around 1920, Miss Ostwald has been confined to a wheelchair because of polyarthritis.

▼ ▼ ▼

THE ORIGIN OF PETROLEUM[1]

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THE origin of petroleum is a challenging and elusive problem that has been the subject of considerable speculation and investigation by chemists, physicists, geologists, and bacteriologists for nearly a century. Their combined contribution to the published literature is vast. Many of the speculations have lost their significance as our knowledge of the composition of petroleum and the geological environment has developed. Although the number of reasonable theories has narrowed greatly in recent years, no theory has yet evolved which explains all of the known facts. The chemical complexity of petroleum, its fluid and hence migratory nature, and the antiquity of even the youngest known oil accumulation combine to make the pursuit of this problem especially difficult.

There are few other problems in petroleum technology that invite as much vigorous and controversial discussion among workers in the field. Perhaps the complex nature of the problem, and the fascinating possibilities of a successful solution of it, account for this. Nonetheless, it is difficult to discuss the matter with many people without being subjected to promotional arguments that often involve rather elastic interpretations of the available facts.

GENERAL CONSIDERATIONS

Any theory about the origin of oil must be in agreement with certain basic geologic conditions as established by widespread observations. The five "posts" usually considered as most important in a "geologic fence" are as follows:

Source Material. Some of the early theories on the origin of petroleum postulated inorganic source material. For example, the action of subterranean waters on metallic carbides was proposed by Berthelot (*1*) in 1866 as the mechanism by which oils were formed. He had been able to demonstrate that hydrocarbons could be produced in the laboratory by treating iron carbide with water, and he postulated that since iron carbide had been found in meteorites, such materials were present in the earth and were available for hydrocarbon-producing reactions. About the same time, Mendeleev (*2*) showed that CO_2 and water could be made to react with alkali metals to yield hydrocarbons. These inorganic theories continued to be supported, in part, as late as 1938 by Lind (*3*), who thought that the great complexity of petroleum could be accounted for only by a series of reactions on simple source materials.

There is general agreement now, however, that oil has an organic origin. This is supported by the close association which exists between petroleum and sediments which are relatively high in organic content. In fact, no oil pools have been found in traps and reservoirs in geologic sections that are devoid of or lean in organic matter. While it is true that petroleum-like materials can be formed in the laboratory from inorganic substances, the occurrences and distribution of these substances do not fit geological history. In addition, it has long been known that most crudes are optically active. Since no optically active compounds are known that are not formed by living organisms, it seems reasonable to conclude that organic matter must constitute an important source material for petroleum. Further to this point, Oakwood (*4*) has made the significant observation that optically active compounds recovered from kelp have the same sign and the same molecular weight range and distribution as the optically active hydrocarbons in petroleum. Another important piece of evidence supporting the general theory that petroleum is of organic origin is the discovery by Treibs (*5*) that petroleum contains both animal and plant type porphyrins (*i. e.*, hemin and chlorophyll).

The work of Trask (*6*) and others has shown that organic material is very widespread in sediments all over the world. The organic content of recent nearshore sediments varies from 1 to 7 per cent, with an over-all average of 2.5 per cent. The organic content of oceanic sediments is somewhat lower, averaging 1.0 to 1.5 per cent. If all of this material were converted to petroleum, it would be enough to account for far more petroleum than is known in the world.

Trask and Wu (*7*) were unable to find liquid hydrocarbons in recent sediments although they did find significant amounts of solid paraffins. These hydrocarbons had a melting point of 62°C. which would put the average number of carbon atoms per molecule between 20 and 30. On the other hand, Dr. Paul V. Smith (*8*) has reported finding liquid hydrocarbons in recent marine sediments and has concluded, as a result of this, that petroleum is being formed in recent sediments today. Others have obtained similar results but disagree with his conclusion. In any event, his work is very interesting.

The general geographic and geological relationship between coal and oil has led some investigators to believe that these substances have a common origin. Hubbard (*9*), Terres (*10*), and Craig (*11*) have all contributed significantly to this belief. Further support of this is indicated by the fact that cresylic acids obtained from coal tar and from cracked petroleum stocks are

[1] Presented before the New York Section of the American Chemical Society, Dec. 11, 1953.

similar in physical properties; also, the aromatics from crude oil are similar to those obtained from coal tars.

Environment. Ninety-nine per cent of the world's oil fields are associated with sediments known to be deposited in a marine environment. This is very persuasive evidence that petroleum genesis occurs largely in a marine type of environment. Further to this point, rocks known to have been deposited in a fresh water environment contain little or no petroleum, even though they may have a lithologic character similar to that of marine sediments.

Most oil-field reservoir rocks are hydrophilic. The interstitial water which coats the pore walls commonly has high chloride content, which in some cases is much higher than that of sea water. This is also true of the bottom and edge water of most oil fields. Occurrences of relatively fresh interstitial and edge water are believed to be exceptions due either to dilution by meteoric waters or migration of oil into beds already saturated with fresh water.

Temperature. Geologic history indicates that most oil basin temperatures have been low throughout geologic time. The maximum temperatures have probably been approximately 150°C. for most oil basins, with temperatures slightly higher in unusual cases. The presence of chlorophyll derivatives in petroleum is regarded as good evidence that it has had a low-temperature history, probably not in excess of 200°C. This is further borne out by the presence of complex nitrogen compounds (*12*), unstable above 200°C., in California and other crudes. It is the general belief that the temperature history of petroleum formation begins with the temperature of the ocean water and increases in general only with the continued increasing thickness of deposits and the temperature gradient of the area.

Pressure. The pressures that exist in oil-bearing formations today vary from a few hundred to about 7,500 lbs./sq. in. There is no reason to expect that petroleum was formed under different pressures than are found in oil-bearing formations at present. The role of pressure in the formation of oil is generally considered to be secondary, at best.

Time. Accumulations of petroleum occur in rocks of all ages from the Cambrian to the Pliocene. This places the order of magnitude of the time factor in petroleum genesis, maturation, and accumulation in the range of 1 to 500 million years. Within this range there is evidence to indicate that petroleum composition varies at least qualitatively with the age of the geologic sediments, *i. e.*, petroleum found in the older sediments is usually much more paraffinic than petroleum found in the younger sediments. Barton (*13*) showed this in his study of Gulf Coast fields, and more recently McNab, Smith, and Betts (*14*) have shown the same thing in a statistical study of over 200 crude petroleums. However, composition may also be related to nature of the source material and depositional environment as indicated by Hunt (*15*) in his study of Wyoming crudes. There is little or no evidence to show the formation of petroleum since the Pliocene age, with the possible exception of the work of Dr. Paul V. Smith.

THEORIES OF PETROLEUM GENESIS

Although the major hydrocarbon groups which go to make up petroleum are found widespread in living organisms and in the organic debris trapped in recent sediments and soils, the time, place, and mechanism by which these residues become liquid mixtures sufficiently like petroleum in chemical composition and physical properties to be called proto-petroleum are not known with any reasonable degree of certainty. There are, of course, a number of theories as to how this transformation might take place. The four most widely known of these theories are discussed briefly below.

Thermal Decomposition. The theory that petroleum is formed by thermal decomposition of fatty oils is one of the earliest theories of petroleum genesis. This idea was advanced by Warren (*16*) in 1863, and later by Engler (*17*). It was assumed that the unsaturates formed by thermal decomposition of fatty oils would be polymerized to form high boiling hydrocarbons such as are found in petroleum. Naphthenes and aromatics would result if the temperatures were high enough. The widespread occurrence of fatty oils in nature provided an ample source of raw material.

There are many facts as we know them today which tend to refute this theory. For example, oil reservoir temperatures are entirely inadequate for the thermal reactions described above. Also the presence of thermolabile substances in petroleum, including chlorophyll porphyrins, is not consistent with this theory. Further, the occurrence and distribution of individual hydrocarbons in petroleum have no correlation with the thermodynamic stability of hydrocarbons (*18*). As a result of these and other facts we have developed over the years, regarding petroleum and the sediments in which it is found, the thermal decomposition theory for formation of petroleum is not widely accepted today.

Bacteria. The formation of petroleum hydrocarbons in recent marine sediments by bacteria has not been demonstrated, although it is known that the sediments do contain methane-producing bacteria (*19*) and that certain bacteria found in sediments contain minute amounts of hydrocarbon as a part of their cell substance (*20*).

It can be demonstrated in the laboratory that anaerobic bacteria convert fatty acids into methane in large quantities. However, the production of higher paraffin homologues is of the order of only a very few parts per million. It should be cautioned that these observations are not indicative of anaerobic bacterial activity in general, or of such activity in sedimentary rock. Both aerobic and anaerobic bacteria are found in plentiful amounts in recent sediments, but usually in numbers decreasing with depth. Data on the presence of bacteria in ancient sediments are very limited. Most bacteria have a temperature tolerance of less

than about 75°C. Pressure tolerances are considerably greater, at least for certain strains of bacteria. ZoBell (*21*) has described bacteria that grow at a pressure of 9000 p. s. i., and has even indicated that temperature tolerances may be extended for some bacteria at higher pressures.

The presence of hydrocarbon material in bacterial cell substance has been cited by ZoBell (*22*) and Stone (*20*). Some doubt exists relative to the reliability of the analytical data obtained in this work because of the extremely small amounts of material available for analysis. However, the data, such as they are, indicate that the hydrocarbon material is generally paraffinic in nature.

The general belief today is that bacterial activity is probably involved in petroleum genesis, but the extent to which this occurs is debatable. Under highly artificial conditions hydrocarbon formation by bacteria has yielded only small amounts of paraffinic hydrocarbons, other than methane, and practically none of the myriad of other constituents of petroleum. The conservative viewpoint is that bacterial action is limited to producing organic material more closely resembling petroleum than the original material, and that the final stages of petroleum genesis are physicochemical.

Radioactivity. Radioactive processes have been considered as one of the possible mechanisms involved in the genesis of petroleum because of the widespread occurrence of radioactivity in natural rocks, and the known effects of alpha radiation on gaseous hydrocarbons and fatty acids. Lind (*23*) has shown that liquid hydrocarbons are formed by the action of alpha radiation on gaseous hydrocarbons, and Whitehead, Sheppard, and others (*24, 25, 26*) have shown that small amounts of paraffin hydrocarbons can be produced by alpha bombardment of fatty acids. In either case, however, the yields are extremely low, and the suggested reactions are not consistent with the low intensity of most natural radiation. In addition, both reactions produce large amounts of hydrogen gas, the general absence of which in natural gas cannot be accounted for unless it be assumed that the hydrogen reacts further with the produced hydrocarbons in some manner.

The general effect of alpha radiation on hydrocarbons themselves is to knock off hydrogen atoms. If this effect occurred on any significant scale, petroleum would become progressively heavier and poorer in hydrogen with age. This is entirely opposite to what we know to be the case, with the geologically older oils being generally lighter and richer in hydrogen.

One further fact that argues partly against the radioactivity theory for the genesis of petroleum is that there appears to be no relation between the abundance of petroleum and natural gas and the proximity of radioactive minerals.

It is generally conceded that radioactivity may play some part in petroleum genesis but that its role is a minor one at best.

Catalytic Activity. The belief that catalytic activity of certain natural minerals has played an important role in the genesis of petroleum has gained increasing acceptance as we have learned more and more about catalytic processing in petroleum refining operations. This theory also does a fair job of taking into account the natural geologic conditions which are believed to exist during the formation of petroleum.

Getling and Frost (*27*) have made important contributions to this theory. They found that at temperatures between 150° and 200°C. organic compounds, in the presence of certain clays, may undergo reactions of dehydration, isomerization, disproportionation of hydrogen, polymerization, condensation, and decomposition leading to the formation of petroleum-like hydrocarbons from alcohols, esters, ketones, and other organic compounds. Brooks (*28, 29*) has considered in detail the carbonium ion theory for certain low-temperature catalytic processes in current use in petroleum refining, and suggests that this mechanism could account for low-temperature formation of the multiplicity of hydrocarbons found in petroleum. He suggests further that the variation in catalytic activity in the sediments may account for the differences in crude oils that we find. As evidence in support of this general theory of petroleum genesis, he cites the low-temperature history of petroleum, the widespread occurrence of catalytic minerals in petroleum-bearing sediments, the general stability of paraffins except in the presence of catalytic agents, and the presence of aromatics and cycloparaffins in petroleum, formation of which is very difficult to explain at low temperatures unless catalytic agents are present.

While these arguments tend to be more convincing than those offered for some other theories of petroleum genesis, factual data are difficult to obtain because of the geological time factor. It does appear reasonable, however, on the basis of our present knowledge of catalysis, to conclude that the catalytic activity of natural minerals may play an important role in the genesis of petroleum.

SUMMARY

In summary, we note that the theories for the origin of oil are many and conflicting. From the facts now known we can reasonably conclude that petroleum is of organic origin, derived from both terrestrial and marine organic matter, and that the genesis occurs at temperatures less than 200°C. The genesis appears to involve mainly the conversion of organic matter to petroleum by a combination of physical and chemical factors, perhaps aided appreciably in the early stages by bacterial action. There may be some contribution by way of concentrating the hydrocarbons produced by living organisms. The duration of the transformation process is unknown, for no one yet has traced the steps from formation of organic residues in recent sediments to the first appearance of a liquid mixture having the chemical composition and physical properties of crude oil. It

may be more significant than we realize that the youngest known accumulation of oil is found in rocks of Pliocene age, one million years old.

ACKNOWLEDGMENT

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THE following undergraduates, for outstanding scholarship in their respective colleges, were awarded subscriptions to the JOURNAL OF CHEMICAL EDUCATION by the Louisiana Section of the American Chemical Society Auxiliary: Barbara Broussard of Loyola University; Ethel Marie Mendow of St. Mary's Dominican College; Dianne Noblet Calongne of University College, Tulane University; and Linda Lee Smith of Newcomb College, Tulane University.

THE LIEBIG-PASTEUR CONTROVERSY

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It is now some fifty-odd years since Büchner resolved the famous Liebig-Pasteur controversy regarding the nature of alcoholic fermentation that had been raging across political boundaries on the European continent during the last half of the nineteenth century. The strong emotional overtones engendered by the protracted debate of these famous personalities had the incidental value of inspiring each of the men to his best achievements. Both Liebig and Pasteur died as bound to their respective theories as when they lived, Pasteur having died but two years before the elusive causal agent of alcoholic fermentation was accidentally uncovered by Eduard Büchner.[2] The legacy of this famous controversy to the twentieth century is the amazing growth of biochemical science, whose foundations rest on a synthesis of the work of these outstanding investigators.

VITALISM

As the controversy expressed itself in the nineteenth century, the issue was whether vitalism might be invoked as an explanation of certain groups of chemical reactions grouped together under the designation of "fermentation reactions." The roots of the controversy went back to the earlier historical foundations of organic chemistry where vitalistic and nonvitalistic schools of thought had their origin in a discussion of the mechanism of chemical reactions. In 1828 Wöhler, the closest friend and colleague of Liebig, had succeeded in exercising the ghosts of vitalism from the major portion of organic chemistry by his now classical synthesis of urea without "vital" intervention. Liebig's ideal remained to carry on Wöhler's tradition of explaining the products of living activity in terms of a theoretical chemical system. For Liebig, fermentation reactions, because of their somewhat more intractable complexity, constituted no exception to the ever present ideal of chemical explanation. In the twenty-ninth volume of the *Annalen der Pharmacie*, published in the year 1839, Liebig satirized the vitalistic theory of alcoholic fermentation:

> I am enabled to reveal a new theory of vinous fermentation. (With the aid of a microscope anyone can notice animalcules present in a fermenting liquid.) . . . The shape of these animals differs from that of any known species, for they possess the profile of a Beindorf distillation apparatus (with the condenser omitted!) . . . These animalcules gulp sugar, excrete vinous spirits by way of their intestinal tracts, and carbonic acid by way of their urinary organs. . . !

Turpin, whose studies were the object of Liebig's humor in this passage, Cagniard de la Tour, Schwann, and Kützing were the unacknowledged forefathers of Pasteur's viewpoint. It was they who first eloquently expressed the sum and substance of Pasteur's dictum: the phenomena of alcoholic fermentation were inexplicable without resort to a vitalistic hypothesis. But Pasteur aligned himself with his prototypes by way of a differing genetic trail.

OPTICAL ACTIVITY

Pasteur's earliest work concerned optically active organic compounds. He succeeded in offering an acceptable explanation of optical activity in the molecular asymmetry of optically active compounds. But he sought a "deeper" explanation of optical activity; he stated that compounds owe their molecular asymmetry to some mysterious transposition of the asymmetry of the earth.[3, 4] Though a sphere is symmetrical when stationary, Pasteur emphasized the fact that the mirror image of a *revolving* sphere was nonsuperposable. Thus the sun's rays as they shine upon the earth do not have the same direction in object and image, *i. e.*, they are asymmetrical. Therefore, an asymmetrical quality is imparted to chlorophyll in plants which use the sun's energy, and, hence, the train of optically active organic compounds is initiated.

As an obvious corollary to this theory, there was a causal connection stipulated between optically active organic compounds and living organisms: optically active compounds can only be produced by the operations of living organisms. Thus, whenever there exists evidence of the formation of optically active compounds, one can infer the presence of living organisms.

It is rather difficult to believe that all of Pasteur's later work in fermentation had its origin in this erroneous theory. Yet such was the case.[5] For example, it was the production of a small quantity of optically active amyl alcohol in alcoholic fermentation that initiated Pasteur's conviction that fermentation reactions require a living precursor.[6] His firm belief in this reasoning led Pasteur to focus his penetrating attention on the discovery and study of the responsible microorganisms. The French vinegar and wine factories became very prosperous as the result of the better

[1] At present on military leave of absence with the U. S. Army at Army Chemical Center, Maryland.

[2] Büchner, E., *Ber.*, **30**, 117 (1897).

[3] Duclaux, E., "Pasteur: The History of a Mind," W. B. Saunders Co., Philadelphia, 1920, p. 30.

[4] Pasteur, L., "Recherches sur la dissymétrie moléculaire des produits organiques naturels," 1860.

[5] Dubos, R., "Louis Pasteur," Victor Gollancz, London, 1951, p. 125.

control that now became available over the vinous and acetic acid fermentation processes. And microbial diseases that afflicted millions were successfully mitigated by the highly empirical processes that Pasteur soon devised with the aid of this working hypothesis.

We may easily summarize the essentials of Pasteur's conceptual scheme. The fermentation and putrefaction processes of organic matter are brought about through the agencies of highly specific microörganisms. By varying the conditions under which they carry on their vital activity (*i. e.*, by varying both the quantity and quality of their nutriment, the presence of competitive or enemy bacteria, the presence or absence of air) a definite control can be maintained over the products of the reactions. Appropriate modifications and qualifications of this working hypothesis made it applicable to a study of microbial activity.

To point out the instances during Pasteur's lifetime when the inaccuracies of his original assumptions led him astray would sound trivial in comparison with the astounding fruitfulness of these ideas. For example, it appears picayune to mention that Pasteur refused to recognize an optically active malic acid that had been synthesized in the laboratory because it had not been produced by the intermediary of vital activity.[6] Nor would it appear very significant to call attention to the fact that Pasteur never attempted to incorporate within his theory the nonvital fermentation of amygdalin by emulsin.[7] When weighed on the balance, the immediate fruitful results obviously outweigh the few contemporary discrepancies from truthful fact. Duclaux, Pasteur's biographer, reads a philosophic message into these circumstances when he writes that,

> A new theory in order to be useful and fruitful does not need to have a solid foundation. It is enough that it should be sufficiently well founded to give a new point of view, one which allows the investigator to see things the other way around, and it even happens that some inexact theories may claim an active part in progress.[8]

Yet when Pasteur's arguments are compared with Justus von Liebig's from the more detached perspective of our age, one is tempted to be skeptical regarding Duclaux' peremptory generalizations.

LIEBIG'S THEORY

In its barest outlines, Liebig's theory of fermentation stated that ferments consisted of complex organic compounds containing nitrogen which were in a process of decomposition. This decomposition of the ferment into various less complex compounds resulted from an atomic motion initiated under the appropriate conditions (such as the presence of oxygen), which shifted the position of the atoms within the compound. The excitation of this atomic motion within the nitrogenous matter was communicable in aqueous media to a variety of other compounds (called fermentescible substances). Thus, many carbohydrates were fermentescible and would decompose into alcohol and carbon dioxide in a solution in which some albuminous matter had been inoculated. Occasions when aldehydes or water instead of alcohol were produced were explained by postulating different degrees of attainment of complete decomposition by the nitrogenous material. The presence of yeast cells in alcoholic fermentation was regarded by Liebig as incidental but, nevertheless, beneficial, for he felt that their presence aided the oxidation of the decaying nitrogenous matter. He also felt that dead yeast cells would, by their decay, speed up fermentation.

While Liebig never denied the presence of yeast cells that were alive in alcoholic fermentations, he attached no scientific value to an account of fermentation which simply stated that fermentation was caused by living cells. As Liebig said:

> If we ask the microscopic investigators what lactic acid fermentation really is, we receive for a reply the name of a fungus. . . . But one cannot see "theoretical relationships" with a microscope! . . . Observations of this sort are perfectly suited to define certain objects which have taken part in some event, and to direct investigation appropriately; but if one believes that one has completed the job by [calling attention to] the discovered but unexplained object, then one demonstrates clearly that one fails to recognize the value of physiological facts.[9]

In so many words Liebig declared emphatically that there must be no apotheosis of microscopic organisms. Rather, the scientist must seek an explanation for observed phenomena which will fit coherently (or will have the probable potentiality of fitting coherently) into a theoretically developed system. This was the implicit principle which guided Liebig in all his chemical research.

VINEGAR PRODUCTION

The fruitfulness of Pasteur's vitalistic theory has often been forcefully emphasized by his biographers through his handling of the vinegar problem of the French manufacturers. Undoubtedly Pasteur's researches into the biological events associated with the industrial production of vinegar made substantial contributions to the blind empirical techniques until then used by producers. By pointing out the marked correlation existing between vinegar production and the conditions for successful culturing of *mycodermi aceti*, Pasteur enabled the vinegar manufacturers to control their product better. The result was a vinegar economically produced and free from the bad odor and flavor resulting from nonselective bacterial growths. Pasteur's research in this field was unquestionably fruitful in so far as the industrial application was concerned and, also, in so far as the incidentally developed laboratory techniques were concerned. Yet on this very same topic Liebig countered Pasteur's empirical fruitfulness with his own theoretical fruitfulness.

In 1837 Liebig reported[10] the results of some researches that he performed on the problem of vinegar

[6] DUBOS, R., *op. cit.*, p. 154.
[7] CONANT, J. B., "Pasteur's Study of Fermentation," Harvard University Press, Cambridge, 1952, p. 34.
[8] DUCLAUX, E., *op. cit.*, p. 5.
[9] LIEBIG, J., *Ann.*, 153, 44 (1870).
[10] LIEBIG, J., *Ann.*, 21, 113 (1837).

production. Liebig's work preceded Pasteur's on the same topic by some twenty-five years, so that the circumstances and subsidiary problems which faced each investigator in this same problem were markedly different. The analogy of Liebig's work on vinegar with that of Pasteur is, hence, only appropriate to indicate the different goals which two investigators carried before them in considering the significance of the production of vinegar.

In attacking the problem Liebig was interested in selecting those details which helped both to explain how spirit of wine could ultimately result in acetic acid and how this explanation could contribute to the growth of a highly organized conceptual system. Liebig pointed out that the production of vinegar from alcohol proceeds in two stages: the alcohol is oxidized first to an intermediate product, to which Liebig, after a technical examination of its constituents and properties, gave the name "aldehyde" (now called acetaldehyde); then the aldehyde is further oxidized to the final product, acetic acid. By quantitative examination of principal produets and reactants, Liebig could explain the process in terms of the molecules that entered into and were produced in the reaction and give estimates as to the proportional amounts of reactants required to yield a given amount of product. By this examination Liebig had recognized one of a series of chemically important compounds, namely, aldehydes–which was a significant inclusion in the rapidly developing chemistry continuum–had explained its properties and had developed a test for its presence (ammoniacal silver nitrate yielding a glistening coat of pure silver in the presence of aldehyde).

There has been much misunderstanding about the role which Liebig actually assumed for his theory of fermentation. Bitter vituperations have been cast at Liebig by vitalists, who, concerned only with the immediately perceptible results and overwhelmed by Pasteur's vigor and forcefulness, have never bothered to understand Liebig. They abstract from the context of Liebig's life work his formal theory of fermentation with the distorted intention of showing the chauvinistic stubbornness with which he defended it. Yet Liebig was sufficiently broadminded to realize the possibility of his theory of fermentation's being incorrect in some of its details. Liebig wrote in 1839:

> In all natural occurrences we have only guides or tentative hypotheses concerning the operating theoretical relationships; they serve to conceptualize these modes of causation. These conceptual schemes vary with the prevailing ideas of the time; they may be erroneous and may change without in the least affecting the permanence of the theoretical causal relationships. . . .[11]

This statement made in connection with his theory of fermentation showed that Liebig realized its tentativeness. The criteria he used to ascertain the tentative validity of his theory were: (1) reasonable explanation of appropriate observations; (2) the capability of the theory of explaining a large number of chemically similar phenomena; and (3) the capability of the theory of harmoniously fitting into a developing system of coherent conceptual schemes and of satisfying certain principles of investigation (*e. g.*, "no hypothesis that involves recourse to vague vitalistic concepts may be adopted").

[11] LIEBIG, J., *Ann.*, **30**, 364 (1839).

AMYGDALIN

The fermentation of amygdalin by emulsin, yielding prussic acid, sugar, and oil of bitter almonds[12] was much more conveniently explained on Liebig's theory than on Pasteur's, for in this case there were no living cells present to account for the reaction. The thought of attempting to ferment amygdalin with an emulsion of sweet almonds could never have occurred under Pasteur's hypothesis because of the nonliving nature of the ferment. This fermentation was of value to Liebig and Wöhler in their cyanide and benzoyl researches. Further, by considering this fermentation in the light of their hypothesis, they realized that something else besides prussic acid and oil of bitter almonds should be produced. They found it to be sugar and reported for the first time "a member of another new and most important group of substances—the glucosides."[13] Perhaps the greatest usefulness of this theory and the greatest value which Liebig's insistence upon it has had for modern biochemical science is its collocation of all the manifestations of fermentation and its assertion of their relatedness. Pasteur's theory did not incorporate the role of enzymes of digestion, which had long been known (such as the action of ptyalin, diastase, pancreatin, etc.). Liebig's theory embraced digestive enzyme activity, the activity of "unorganized" ferments (like emulsin), and alcoholic, lactic acid, and butyric acid fermentation within its gamut. Their basic interrelatedness for Liebig is well brought out by his statement of 1870:

> It may be that the physiological process stands in no other relation to the fermentation process than the following: a substance is produced in the living cells which, through an operation similar to that of emulsin on salicin and amygdalin, leads to the decomposition of sugar and other organic molecules; the physiological process would in this case be necessary to produce this substance but would stand in no further relation to the fermentation.[14]

Pasteur regarded this statement as a diplomatically couched concession on Liebig's part to his vitalistic theory; but it was, in fact, nothing more than what Liebig had always maintained. One of the everlasting merits of Liebig's theory is thus its retention of enzyme observations and alcoholic fermentation observations within the same conceptual scheme so that further growth in this scheme could be effected by either enzyme or fermentation research. But the greatest merit of Liebig's theory lay in its insistence on a chemical explanation for fermentation, an explanation which could

[12] LIEBIG, J., *Ann.*, **22**, 1 (1837).

[13] SHENSTONE, W., "Justus von Liebig," The Macmillan Co., New York, 1895, pp. 34–5.

[14] LIEBIG, J., *Ann.*, **153**, 6 (1870).

coherently fit into the chemical system of conceptual schemes, and the impetus which it gave to later work in this direction.

ENZYMES

The Liebig-Pasteur controversy continued on the verbal level, owing to the absence of further corroborating evidence, until 1897, when Eduard Büchner's[15] evidence was brought to light. Büchner had succeeded in extracting from living yeast cells a juice which had no living cells of any kind in it, yet which could initiate an alcoholic fermentation by being brought into contact with sugar. Büchner called this enzyme zymase, thus unequivocally bringing alcoholic fermentation into the general enzyme theory which had been developing since the discovery of diastase in 1833. Pasteur's basic thesis that fermentation could never take place without the presence of a living agent was disproved.

In 1926 J. B. Sumner[16] reported the isolation and crystallization of the enzyme urease, thus indicating that the cause of fermentative reactions was a definite, though complex, chemical compound. The chemical theory of fermentation which Liebig had insisted upon was now making great headway. Harden[17] has described alcoholic fermentation as a very complex chemical reaction proceeding in several stages. Phosphorylated sugar is split by hexokinase, an enzyme, into triosephosphates. Among these appears glycerin aldehyde diphosphate, which reduces acetaldehyde to alcohol. At the same time it is oxidized to diphosphoglyceric acid, which is transformed into pyruvic acid. Pyruvic acid decomposes into acetaldehyde and carbon dioxide gas, and the acetaldehyde is reduced to alcohol by reacting with more glycerin aldehyde diphosphate. The detailed mechanism of this reaction includes the functions of a coenzyme and a great variety of intermediary enzymes.

This line of work has been continued and is at present actively being pursued in the research of such men as the 1953 Nobel laureates, Hans Krebs and Fritz Lipmann. The "citric acid cycle," explaining chemically aspects of the metabolism of the living cell, and the isolation and chemical synthesis of coenzymes are but two of the many biochemical investigations that owe their deeper purpose as well as their methods and techniques to the results of the colorful intellectual sparring of Louis Pasteur and Justus von Liebig.

ACKNOWLEDGMENT

The author wishes to thank Professor Fletcher G. Watson of Harvard University for his critical reading of the manuscript.

[15] *Supra.*

[16] SUMNER, J. B., *Biol. Chem.*, **69**, 435 (1926*a*).

[17] HARDEN, A., "Alcoholic Fermentation," 4th ed., Longmans, Green, & Co., London, 1932.

CONTRIBUTIONS OF LIBERAL-ARTS COLLEGES TO THE JOURNAL OF CHEMICAL EDUCATION, 1934–53

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A STUDY has been made of the articles from liberal-arts colleges contributed to the JOURNAL OF CHEMICAL EDUCATION during the fifteen-year period 1934–48.[1] A check on the same subject for the succeeding five years discloses a strikingly similar pattern of widely scattered contributions from a large number of institutions, but sustained interest through the years from only a small group. During 1949–53, 68 liberal-arts colleges contributed 110 articles. This constituted again 10 per cent of the material (1010 articles) in this publication on the teaching of chemistry. The seventh (1953) edition of *The College Blue Book* has been used to determine the liberal-arts status of the institutions.

Thirty-nine colleges not in the 1934–48 study appeared in the issues of the last five years, but 79 institutions listed in the 15-year tabulation failed to contribute during 1949–53. Only ten colleges have contributed more than half a dozen articles during the 20 years, but these ten account for one-fourth of all the material from liberal-arts colleges. The ten leading contributors were: Wooster (16), Antioch (14), Furman (11), Grove City (9), Hollins (9), Monmouth (9), Haverford (8), Colgate (7), Dakota Wesleyan (7), and Queens (7). This activity actually represents the work of a very few particular individuals.

[1] SAMPEY, J. R., J. CHEM. EDUC., **27**, 69 (1950).

THE PLATINUM-GROUP METALS

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THE platinum-group metals comprise platinum, palladium, iridium, rhodium, ruthenium, and osmium. Platinum is the principal member of the group, but each of these metals has many important and steadily growing applications, in the compact, pure metallic state, and in the form of a wide range of alloys of members of the group; and in combination with gold, silver, and various base metals, in the finely dispersed metallic state, and as pure chemical salts.

Native platinum was first discovered as early as the sixteenth century in Colombia by Spanish travelers. It was named Platina de Pinto in reference to small silver-like particles found in the auriferous placers of the River Pinto. For centuries very little interest was taken in the metal owing to its high melting point which made it difficult to work, and it was thrown away as useless until in the eighteenth century it began to appear in spurious coins struck from the crude metal and coated with gold in counterfeit of Spanish doubloons. The government forbade its export from South America and ordered it to be thrown into the sea to prevent its use for the adulteration of gold.

In 1741 samples were taken to England and the remarkable properties of the metal at once attracted attention and led to investigations whereby five additional metals were discovered in the complex native metal. Smithson Tennant discovered osmium and iridium in 1802, and in the following year W. H. Wollaston revealed rhodium and palladium, while ruthenium was finally announced by C. Claus in 1845. It was rather natural that osmium and iridium received the earliest attention, as native platinum always yielded some very dense acid-insoluble residue. Palladium was discovered in the course of investigations of gold from Brazil which, being brittle, did not find ready acceptance. Ruthenium went undiscovered until heavy black grains contained in platinum concentrates from Borneo attracted attention.

The names given to the metals originated as follows: platinum, from the Spanish *plata*, meaning silver; iridium, from the Greek *iris*, a rainbow, owing to the wide range of colors exhibited by its salts; osmium, from the Greek *osme*, a smell, in reference to the pungent odor of its volatile tetroxide; ruthenium, after *ruthen*, for Russia; rhodium, from the Greek *rodon*, a rose, a color exhibited by many of its salts; palladium, after the planet Pallas.

Interest shown in platinum led to the exploitation of the Colombian deposits in 1778 and these remained the only source until the discovery of extensive deposits in the Urals in 1823. Within a year Russia became the world's principal producer of alluvial platinum, a position still maintained. Rising prices stimulated search for the metal and it was found to be widely distributed, though often in small quantities. Toward the latter part of the nineteenth century substantial recoveries of native platinum were made from the Tulameen River, British Columbia, and from southeastern Borneo, but these deposits seem largely to have been worked out. Tasmania was an important source of osmiridium between the two World Wars, but here too the deposits appear to have been worked to near exhaustion. Between 1927 and 1940 significant recoveries of the native metals were obtained from eluvial deposits in Ethiopia. Domestic production has been quite important during the past 15 years owing to the activity at Goodnews Bay, Alaska.

For some years, however, the bulk of the world's supply of the platinum metals has come from the nickel-copper ores of Sudbury, Ontario, and Rustenburg, South Africa. While the platinum metals are present in both ores to the extent of only small fractions of the ounce per ton, the large volume of ore treated results in very substantial production, equivalent to perhaps 70 per cent of world platinum production, at the present time, together with a large amount of the other metals of the group.

The ores of Sudbury are richer in copper and nickel than those of South Africa, but the latter contain a higher concentration of platinum metals. Thus it might be said that platinum is a by-product of the base metal obtained from the Canadian ore, while that from South Africa is worked primarily for the platinum metals, with base metals forming a by-product.

MINERALS OF THE PLATINUM METALS

Native platinum occurs in steel-gray grains of specific gravity from 14 to 19 depending on the composition. Large nuggets are rare, although three very large specimens were recovered many years ago, in the Nizhni-Tagilsk District of the Urals, weighing $25^1/_2$ pounds, 21 pounds, and $11^1/_2$ pounds, respectively; commercial concentrates will usually pass through 10 mesh. Individual grains show a very wide range of composition in a single deposit, but some analyses of commercial concentrates from various parts of the world are given in Table 1.

The gold is usually present in separate grains containing some silver. Iron is always present from 2 to 16 per cent as magnetite and chromite, while copper is

TABLE 1
Examples of the Composition of Native Platinum Concentrates

	Russia, %	Colombia, %	Ethiopia, %	Alaska, %	New South Wales, %	Sierra Leone, %	Yukon, %	California, %	Oregon, %	British Columbia, %	Borneo, %
Platinum	70.74	84.97	73.45	73.20	79.89	77.10	73.15	85.50	51.45	72.07	82.60
Palladium	0.24	0.70	0.22	0.33	0.26	1.41	0.29	0.60	0.15	0.19	0.30
Iridium	1.99	1.16	0.30	2.36	2.03	0.65	1.76	1.05	0.40	1.14	0.66
Rhodium	0.79	0.79	0.62	0.96	0.47	1.13	0.96	1.00	0.65	2.57	...
Osmiridium	0.42	0.42	0.67	12.24	6.72	2.70	7.48	1.10	37.30	10.51	3.80
Gold	3.05	0.99	3.48	0.75	0.14	0.03	2.33	0.80	0.85	...	0.20

contained from traces up to 5 per cent. Small amounts of a number of minerals associated with alluvials are present depending on the efficiency of the gravity separations.

Osmiridium is the name given to naturally occurring alloys of iridium and osmium, found as irregular grains, or intergrown with native platinum, ranging from tin-white to steel-gray in color; specific gravity from 18.5 to 20.5.

Tasmania was at one time an important source of this mineral, but the largest production in recent years has been the by-product of gold mining operations in South Africa and that recovered in the course of refining native platinum from Alaska.

Chromite is the usual base-mineral impurity. It is notable of the native alloys that ruthenium is almost entirely associated with the osmium-rich series and palladium with the platinum-rich series, while iridium and rhodium occur in both phases.

Native iridium is a rather rare mineral occurring with native platinum in the Urals and Brazil. Platinum and iridium are the major constituents as shown in the following assay of a sample from Brazil: Pt, 55.44 per cent; Ir, 27.79 per cent; Pd, 0.49 per cent; Rh, 6.86 per cent; Fe, 4.14 per cent; Cu, 3.30 per cent.

Allopalladium, a rare mineral found in the Hartz Mountains, consists chiefly of palladium, with small amounts of platinum, rhodium, iridium, and mercury. It forms silver-white hexagonal plates.

Porpezite, found in Brazil, is a natural alloy of gold with about 10 per cent of palladium.

Potarite is a palladium mercuride, PdHg, found as small octahedral crystals in the Potaro River and neighboring district of British Guiana.

Sperrylite, $PtAs_2$, forms small silver-white cubic crystals with a brilliant luster. It was discovered in 1889 in the copper-nickel ore of the Vermillion mine at Sudbury, Ontario, and reported subsequently in the sulfidic platinum ore of the Bushveld Complex in South Africa. Crystals up to 1.85 cm. have been found in the pegmatitic deposits of the Potgietersrust district.

Cooperite (PtS) and *Braggite* (Pt, Pd, Ni)S, both tetragonal steel-gray crystals, are important constituents of the South African deposits. *Laurite* (RuS_2) occurs with the preceding two minerals in the form of small friable black octahedral grains; it was originally noted in platinum concentrates from Borneo.

Stibiopalladinite (Pd_3Sb) occurs as whitish grains in association with sperrylite in the Transvaal.

MODE OF OCCURRENCE

The platinum metals occur principally in one or other of three associations:

(1) Alluvial and eluvial placers, as, for example, in the Urals, Colombia, British Columbia, Oregon, Tasmania, Alaska, and Ethiopia.

(2) Olivine-rich rocks and other ultra-basic igneous rocks, as at Onverwacht in the Transvaal and at Nizhni Tagil in the Urals.

(3) Nickeliferous pyrrohotite, associated with gabbro and related basic igneous rocks as in the Merensky Horizon of the Bushveld Complex in the Transvaal and at Sudbury, Ontario.

A small but steady production of the platinum metals arises from the treatment of copper sulfide ores mined in the U. S. A., and the Belgian Congo, and also as a by-product of gold refining.

EXTRACTION OF PLATINUM METALS

The nickel-copper ore of Sudbury, Ontario, is primarily worked for the nickel and copper content. The precious metals present in small proportion become concentrated in the crude nickel during various smelting operations. When the bulk of the nickel is removed from the crude metal, either by volatilization as the carbonyl or by electrolysis, a further concentration of the platinum metals is effected. The concentrates may contain at this stage some 5 per cent of platinum metals, 0.5 per cent of gold, and 15 per cent of silver together with a very large number of other elements in variable ratio, but principally copper, nickel, iron, silica, lead, antimony, selenium, tellurium, alumina, and combined oxygen.

The South African ores, also containing the platinum metals in small proportion, are worked primarily for these metals, the nickel and copper being by-products. These ores are first treated by gravity concentration to yield a rich concentrate of platinum minerals, containing up to 40 per cent of the platinum metals, which is roasted to remove sulfur, arsenic, etc. The tailings are subjected to flotation, the remaining precious minerals being recovered with the copper-nickel-iron sulfides, which are smelted to a copper-nickel matte containing some 50 ounces of precious metals per ton.

TABLE 2
Some Examples of the Composition of Osmiridium

	South Africa, %	*Tasmania,* %	*Russia,* %	*Colombia,* %	*Russia,* %	*Alaska,* %	*Australia,* %	*California,* %
Osmium	33.83	45.55	23.01	35.10	48.85	16.75	33.46	43.40
Iridium	28.68	42.24	70.36	57.80	43.94	67.48	58.13	53.50
Ruthenium	12.51	7.92	...	6.37	4.68	1.47	5.22	0.50
Platinum	8.62	1.91	0.41	...	0.14	10.70	...	...
Rhodium	0.43	0.25	4.72	0.63	1.65	3.60	3.04	2.60
Gold	0.50	0.01	...	...	...	...	...	...

The matte is smelted in reverberatory furnaces with salt cake to effect a separation of copper from nickel sulfide. The latter carrying the platinum metals is reduced with powdered coal in a reverberatory to metallic nickel, which is cast into anodes and refined electrolytically. The anode slime is similar to that from the operations on Sudbury ores.

Similar residues are obtained, but in less notable amounts, from the refining of certain other copper and gold ores. Before any attempt is made to extract the platinum metals it is necessary to remove the bulk of the base metals, and these being so variable in proportion and number, a great variety of techniques are employed.

One of the many advantages of platinum is its high scrap value, and accordingly when it becomes unfit for use for any reason it finds its way back to refineries. Such secondary metal may be in a variety of forms from heavy stock to finely divided spent catalysts, and is treated by suitable means to obtain a material in which the platinum metals predominate.

The various forms of platinum-metal-rich material are treated by wet methods, the first general separation being made by attack with aqua regia, the rate and extent of solution depending on the composition and physical character of the material. The acid-insoluble is fused with oxidizing fluxes, followed by distillation of osmium and ruthenium, leaving iridium, rhodium, and base metals behind.

The chloride solutions of the platinum, palladium, iridium, rhodium, and gold, after removal of nitric acid, are separated from each other and from the base metals present by fractional crystallization of their salts. Modern methods result in a high standard of purity of the sponges obtained on calcination of the final salts. Platinum of 99.95 to 99.99 per cent purity is a matter of routine production and for special purposes metal is refined to spectrographic quality.

TABLE 3
World Production of Platinum Metals (in Ounces Troy)

	Prior to 1917	*1916*	*1922*	*1926*	*1932*	*1937*	*1942*	*1948*
Native platinum and osmiridium								
Russia[a]	7,000,000	63,900	27,199	92,688	100,000	100,000	100,000	125,000
Colombia	700,000	25,000	40,000	45,926	40,478	29,315	49,163	40,047
Union of South Africa[b]	.....	....	762	14,951	14,289	5,790	6,685	5,520
Tasmania[b]	.....	222	1,174	3,173	785	586	202	92
Canada[c]	9,000	60	15	50	59	22	30	....
Ethiopia	.....	....	....	719	8,217	3,376	1,988	460
United States[d]	10,000	750	1,008	286	1,074	10,803	23,213	13,741
Papua and Borneo[e]	175,000	10	100	49	3	28	1	....
New South Wales	.....	82	80	397	336	46	8	....
Sierra Leone	.....	....	....	....	531	308	28	109
Japan	.....	70	150	198	266	....	....	....
New Zealand	.....	....	....	31	....	55	12	....
From copper-nickel ore and other prime refining[f]								
Canada	.....	....	1,677	19,495	64,897	259,184	525,000	269,747
Union of South Africa[g]	.....	....	....	1,822	1,480	39,625	73,210	68,926
United States	.....	....	2,482	11,025	2,844	10,578	9,805	5,512
Belgian Congo	.....	....	....	....	2,025	14,629	....	209

The above figures are chiefly from official government statistics; particular periods selected above serve to show the general rises and declines and relative importance of the various sources of the metal.

[a] Russian production is subject to estimation where round figures are given.
[b] Chiefly osmiridium.
[c] The peak year was 1891 when 2000 oz. was recovered from the Tulameen River, British Columbia.
[d] The increase in production results from operations in Alaska.
[e] The early production was from Borneo.
[f] From all sources combined about 65% is Pt, the balance Pd, Rh, Ir, Ru.
[g] South African production is undergoing rapid expansion at present.

THE VARIATION OF EQUIVALENT CONDUCTANCE WITH CONCENTRATION

A Student Experiment

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ALTHOUGH lacking the precision of null-point methods, conductivity techniques based on measurement of current strength at fixed applied a.-c. voltage give direct and continuous indication of conductivity changes. This fact, coupled with the simple nature and manipulation of the apparatus usually associated with the current-measurement method, renders the latter a valuable teaching aid in elementary physical chemistry.

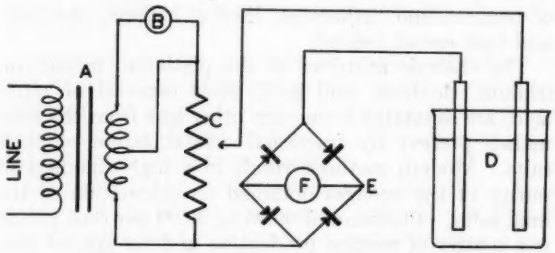

Figure 1. Circuit of Conductivity Apparatus

[1] Present address: University of Minnesota, Minneapolis, Minnesota.

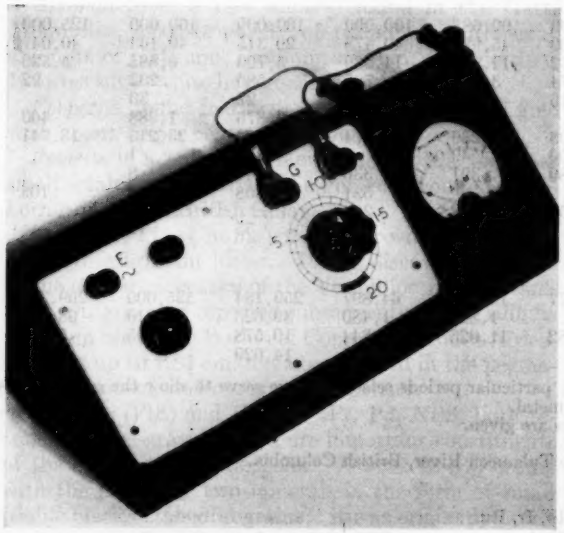

Figure 2. Assembled Control Unit

Circuit arrangements similar to that shown in Figure 1 have been proposed many times previously (for bibliography, see (*3*)). Power from the a.-c. line is stepped down to a few volts by means of bell transformer *A*. One portion of the secondary of the latter energizes pilot lamp *B*, the other being connected across a radio-type potentiometer *C*, of resistance about 15 ohms, which is provided with a roughly calibrated scale. In this manner any a.-c. voltage up to about 2.5 may be applied to electrodes *D*. At fixed applied voltage the current flowing is proportional to the conductivity of the solution; by use of a full-wave "instrument rectifier" *E* (army surplus), the current may be read on a 0–1 milliampere moving-coil d.-c. meter *F*. Such meters having scales lined every 0.02 milliampere and in plastic desk-type mounts are available very cheaply as army surplus, or are not very expensive when of postwar manufacture.

The electrical equipment may be assembled as a compact unit, as shown in Figure 2. The front panel, of $^1/_8$-in. hardboard or plywood, has mounted on it a sheet of drawing board carrying inked scales, binding post inscriptions, etc., and is covered by a sheet of $^1/_8$-in. transparent Lucite. A transparent back is fitted to permit inspection of the wiring arrangements. The baseboard of the unit projects a few inches to the right, thus enabling the milliammeter case to be secured from underneath by a nut and bolt.

To construct the electrode system shown in Figure 3, a length of straight 24 to 28 S.W.G. platinum wire is thrust down each of two melting-point tubes *GG* and sealed in at one end, so that the projection is about 10 mm. long (*3*). Two rings *HH* cut from cycle valve tubing are used to hold the tubes side by side, the assembly being made rigid by fusing glass bead *I* across the extremities of the projecting wires. Light, insulated, flexible connecting leads are then soldered to the upper ends of the wires, short-circuiting being prevented by separating the two joints by a blob of sealing wax. For ease of handling, the electrode assembly may be mounted in a glass collar, as shown at (*a*). The collar may then be snapped into a simple spring clamp made by mounting a "Terry clip" on the end of a piece of hardwood dowel (*6*, *7*). If thus mounted, the rubber rings may be dispensed with. Any drag on the soldered joint is prevented by a tightly fitting rubber stopper.

The electrodes may be bent as shown at (*b*) to permit complete submersion when the liquid depth is small. Platinization, carried out in the usual manner, takes only about two minutes.

Provided that the conductivity of the solution to be examined is not greater than that of approximately centinormal hydrochloric acid, the electrode system gives satisfactory results with the control unit described above. The combination has been used for some years for class experiments in microconductometric titration (*3*) and in reaction kinetics, such as a study of the rate of hydrolysis of tertiary butyl iodide (*4*). A further application of teaching value is to a study of the variation with concentration of the equivalent conductivity of electrolytes. Although results of high accuracy are not to be expected, the experiment is easy to carry out, does not require "conductivity water," and enables the essentially differing behavior of strong and weak electrolytes to be rapidly demonstrated.

Apart from the conductivity equipment, no apparatus other than that required for volumetric analysis is essential, although in the college courses a miniature magnetic-bar stirrer (*5*, *7*) is used for effective mixing without risk of striking the electrode system. As observations are made at very low concentrations, solutions should be free from impurities. Ordinary distilled water is satisfactory, particularly if drawn while the still is running.

PROCEDURE

(1) Prepare a centinormal solution of potassium chloride by weighing out 0.186$_4$ g. and making up to 250 ml. (Some simplification in calculations results from using a solution that is exactly centinormal.) Fill a second flask with the same distilled water as that used in making the solution. Leave both vessels for 30 minutes to acquire the temperature of the laboratory.

(2) Connect up the conductivity apparatus. Dilute 10 ml. of the potassium chloride solution with an equal volume of water, insert the electrodes, and adjust the applied voltage until the meter reading is about 0.96 ma. *Do not alter this voltage setting until observations are complete.* Reject the diluted solution and rinse the electrodes with several portions of distilled water. Pipet 10 ml. of distilled water into a 50-ml. beaker; mount the electrodes so that, although completely submerged, they are clear of the bottom; and start the stirrer. Note the initial meter reading M_0, which is used as a "solvent correction" and should be very small.

(3) Rinse and fill a 10-ml. buret with the potassium chloride solution. Run 0.2 ml. into the beaker and read the meter as accurately as possible (estimate to the nearest tenth of a division). Repeat after further 0.2-ml. additions to a total of 1 ml.; thereafter 0.5-ml. increments up to 5 ml., then 1-ml. increments up to a total of 10 ml. should be made. Note the temperature (°C.) of the contents of the beaker.

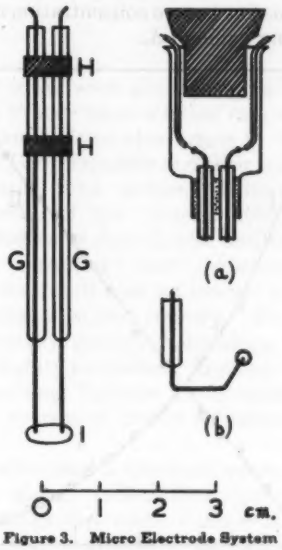

Figure 3. Micro Electrode System

(*a*) Assembly mounted in collar.
(*b*) Side view after bending. (For clarity, the electrode tubes have been drawn slightly separated.)

(4) Record the results on the lines of the table where temperature is 18.5°C. and M_0 is 0.006 ma.

The units of the relative equivalent conductivity are purely arbitrary, the factor 10^2 being introduced to give a value of a few units. Confusion with the *actual*

Vol. added, ml. (V)	*Resulting conc.* (C)[a]	$C^{1/2}$	*Meter reading* *Obs.* (M)	*Corr.* ($M - M_0$)	*Rel. equiv. cond.* (Λ_r)[b]
0.20	1.96×10^{-4}	1.40×10^{-2}	0.056	0.050	2.55
0.40	3.85×10^{-4}	1.96×10^{-2}	0.098	0.092	2.50
		etc.			

[a] $C = (V \times 10^{-2})/(10 + V)$ gram equivalents per liter.
[b] $\Lambda_r = (M - M_0)/(C \times 10^2)$.

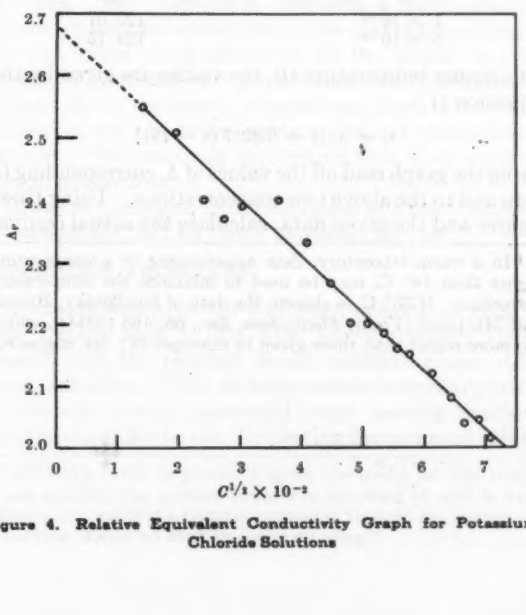

Figure 4. Relative Equivalent Conductivity Graph for Potassium Chloride Solutions

equivalent conductivity (value, a hundred or so reciprocal ohms) is then unlikely.

(5) Plot the relative equivalent conductivity against the square root of the concentration. Although scatter (resulting from line fluctuations, errors in reading the meter, and, particularly with the more dilute solutions, the buret, etc.) is inevitable, the points should lie about a straight line. An actual example is shown in Figure 4. Extrapolate this line to zero concentration and hence obtain the limiting value of Λ_r.

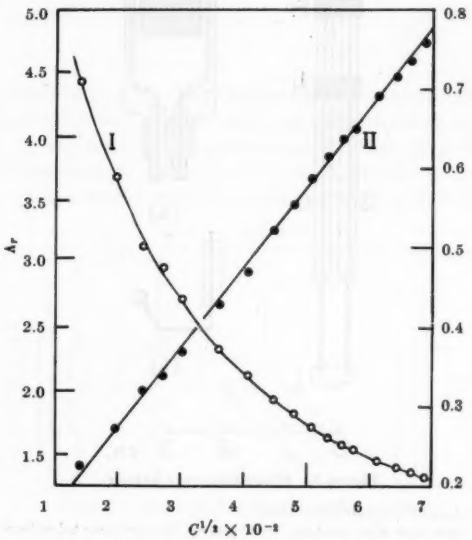

Figure 5. The "Square Root" Rule and Acetic Acid Solutions

Curve I, direct (left-hand scale).
Curve II, reciprocal (right-hand scale).

(6) At 18°C. the actual values (*2*) of the equivalent conductivity of potassium chloride are:[1]

C	Λ
1×10^{-3}	127.07
5×10^{-3}	124.15

At another temperature (t), the values are given by the equation (*1*):

$$\Lambda_t = \Lambda_{18}[1 + 0.0217\,(t - 18)]$$

From the graph read off the values of Λ_r corresponding to zero and to the above two concentrations. Using these figures and the given data, calculate the actual equivalent conductivity of potassium chloride at zero concentration, at 18° and at the actual temperature of the laboratory. Compare the latter result with the accepted value (*2*).

(7) Repeat the experiment, using 0.01 N acetic acid solution in place of potassium chloride solution, suitably resetting the applied voltage. Since a weak electrolyte does not obey the "square root" rule, a nonlinear graph will result. Construct a second graph by plotting the *reciprocal* of Λ_r against $C^{1/2}$. In this case, a straight line should result. Typical results are depicted in Figure 5.

I am indebted to my colleague, Mr. P. Heath, B.Sc., A.R.I.C., for the following explanation of the apparent linearity of the "reciprocal conductivity" plot obtained with acetic acid.

On replacing α, the degree of dissociation, by the conductance ratio Λ/Λ_0, the Ostwald dilution equation

$$\alpha^2\, C/(1 - \alpha) = K \qquad (1)$$

may be rewritten

$$C/K - \Lambda_0^2\,(1/\Lambda - {}^1/_2\Lambda_0)^2 + {}^1/_4 = 0 \qquad (2)$$

Writing $C^{1/2} = x$ and $1/\Lambda = y$, equation (2) becomes

$$x^2/K - \Lambda_0^2\,(y - {}^1/_2\Lambda_0)^2 + {}^1/_4 = 0 \qquad (3)$$

This equation, which is that of a hyperbola, may also be expressed as

$$y - {}^1/_2\Lambda_0 = (x^2/K + {}^1/_4)^{1/2}/\Lambda_0 \qquad (4)$$

If C, the equivalent concentration, is considerably greater than K, the dissociation constant of the acid, the numerical constant becomes negligible and (4) may be approximated to the form

$$y - {}^1/_2\Lambda_0 \cong x/(\Lambda_0\, K^{1/2}) \qquad (5)$$

The final equation, which is also that of one of the asymptotes of the hyperbola, is of the required linear form.

The experimental data may of course be treated in other ways. The present method is very suitable for the direct contrast of weak and strong electrolytes.

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(2) "International Critical Tables," 6, p. 234.
(3) Stock, J. T., *Metallurgia*, 42, 48 (1950).
(4) Stock, J. T., *School. Sci. Rev.*, 31, 336 (1950).
(5) Stock, J. T., and M. A. Fill, *Chem. Age (London)*, 63, 236 (1950).
(6) Stock, J. T., and M. A. Fill, *School Sci. Rev.*, 33, 3 1 (1952).
(7) Stock, J. T., and M. A. Fill, J. Chem. Educ., 31, 144 (1954).

[1] In a warm laboratory, data appertaining to a temperature higher than 18° C. may be used to minimize the temperature correction. If 25° C. is chosen, the data of Shedlovsky, Brown, and MacInnes (*Trans. Electrochem. Soc.*, 66, 165 (1934)), which are more recent than those given in reference (*2*), are suggested.

LAVOISIER'S PROPOSALS FOR FRENCH EDUCATION

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THE "Reflections on Public Instruction," set down in a report to the National Convention of France in 1793 by Antoine Lavoisier, is apparently mentioned nowhere in the literature of education. It is strange that this should be so, since the plan is characterized by a great humanitarianism and contains much of what is timeless in educational philosophy.

It might be surprising to learn that Lavoisier should write a quite considerable monograph on educational reform, until one recalls the universality of his interests, particularly in things which concerned the welfare of his country. The fact that he established, near his Fréchines estate, a primary school paid for out of his own pocket shows an early interest in education. It is a safe assumption that his wide knowledge of social conditions, his zeal for national betterment, the incisiveness of his mind, and the breadth of his general culture and vision would equip him to produce a document worthy of his reputation. Readers of Lavoisier's "Reflections" will find this assumption well justified. The qualities listed above guarantee that his plan is worthy of our attention. Following are the circumstances under which it came into being:

In the year 1791 the French National Convention created an advisory committee charged with the duty of encouraging invention and the advancement of the nation's industries. As president of this committee, Lavoisier prepared a number of its reports. Among them was his "Reflections on Public Instruction," destined to be the most important writing done for this committee. The committee, concluding that the government should be advised to organize a system of education for France, asked Lavoisier in July, 1793, to draw up a plan.[1]

Monarchial ideas were already dying in mid-eighteenth-century France when a lethal rain of intellectual "mace-and-chain" blows also began to descend upon them from the Encyclopedists and their contemporaries, thus accelerating their demise. Voltaire, the most devastating critic of the "Ancien Régime," coming under the influence of John Locke and Isaac Newton, succeeded in spreading their influence throughout France, with the result that an intense interest in the sciences was kindled in that country. Physics, chemistry, zoology, botany, geology, mineralogy, and anatomy rose to a new dignity as studies. Because of his interest in the new learning, Voltaire finally came to advance the idea of a system of public education throughout France.

Locke had advocated a system of education in useful and practical things rather than the classics, and Lavoisier's writings show much of this spirit. Rousseau, a disciple of Locke's, supported learning by doing and education through the senses, though he included only the upper classes in his scheme. Shortly before and during the French Revolution many new plans for general education appeared: Turgot, Diderot, and Roland all had much to say on the subject, as did Talleyrand. The Constitution of 1791 declared that there was to be created "a system of public instruction common to all citizens, and gratuitous for all men." In April, 1792, Condorcet proposed a now famous system for national education. The aim of this scheme was the fullest development of all the people in the interest of good and just government, and it included a setting up of primary, elementary, and secondary schools, as well as *lycées* (universities and professional schools). The emphasis throughout was upon science instead of the classics.

It was at this point in the evolution of French educational thought that Lavoisier produced his plan.

LAVOISIER'S PROPOSALS

A human being, writes Lavoisier, is born an empty page (*tabula rasa*).[2] His first learning comes from contact with the physical world, estimating size, distance, and form. Soon he learns some elementary laws of physics, forces associated with moving bodies, equilibrium of fluids, etc., by playing the games of child-

[1] The first draft dealt with both general and technical training, but the final plan, while retaining its original emphasis upon more advanced practical and technical training, gave less attention than originally to general primary education. It was ordered printed by the Convention in August, 1793, 1000 copies in octavo and 2100 in quarto, the latter having an additional "Project" or detailed study of the organization of a national system of schools. The "Reflections" served as an introduction to the actual plan.

In addition to these two government printings, the "Reflections" and a short extract of the "Project" or study appear in "L'École Renovée," Volume I, 1909, pp. 23–30, by JAMES GUILLAUME. The "Reflections" appear alone in SCHEELE AND GRIMAUX, "Lavoisier Statistique Agricole et Projets de Réformes," Paris, 1894, pp. 84–106; the "Project" alone in Volume IV; and both the "Reflections" and the "Project" in Volume VI of "Oeuvres de Lavoisier" (GRIMAUX), Paris, 1893.

[2] Although Locke is generally given the credit for this term, it was actually the ancient Stoics who invented it, and it was Leibnitz who made it a popular expression through his discussion of Locke's "Essay on Human Understanding."

hood: "for children, to play is to learn, and whoever has not played during the first years of his childhood has never become a man."

Education takes a forward stride when a child learns to supplement his limited physical powers by the use of mechanical tools to produce new effects. Lavoisier shows how the child acquires a knowledge of some of the principles of physics involved in the use of the hammer, nail, knife, and axe, and emphasizes the point that learning is easy if it takes place in the form of amusement. He feels that the main ideas in agriculture, such as a knowledge of soils, fertilizers, etc., are simple and can be quickly taught in the field. Practical geometry is perhaps not more difficult to teach if one directs attention and reflection to children's early ideas of length and size. In that way a basis can be laid for learning how to survey land. From the knowledge which a child gains of thermal expansion, he can be taught about thermometers, and from what he learns of the height of a column of water or mercury which the air will support, he can learn about barometers. Children like to gather flowers, insects, and fish, and then dissect them. We may teach them natural history that way.

Reading and writing are tools which we may use as a preventive against superstition and against the abuse of power. We may even use them as a first guarantee of liberty. Our textbooks should make wide use of pictures so that we may teach the *idea* behind the word, not the word alone.[3]

We can, if we wish, using the method of nature, not only mold men but gradually perfect the intellectual qualities of the human species; in twenty years, what now seems above the capacities of children will seem much too simple, because the knowledge will be familiar to all. Society owes this knowledge to all children; therefore it must be free.

Difficulties make their appearance: individual differences make it necessary to distinguish between those persons who will be public functionaries, studying languages, sciences, and literature, and those who will enter the mechanical fields. For the training of the former we now have colleges and universities; for the training of the latter there are no facilities, since no nation has yet shown interest in the industrial class. The committee (Bureau of Consultation) permits itself some thought on this branch of secondary education.

There are certain knowledges and skills which are fundamental to all men, and therefore to artisans; drawing, for example, is fundamental to all of the arts, which we divide into (*a*) mechanical and (*b*) chemical. This leads to two courses of public instruction. Mechanical arts deal with the work of tools and machines upon wood, metal, and stone. No methodical elementary treatise has yet been written on practical mechanics, because this science does not yet exist. The instructor will teach elementary graphic geometry by use of rule and compass, measurement of surface and solid, the making of projections, and thus the rules of perspective, of stone-masonry, and of carpentry.

Chemical arts can be taught through the description of the properties of natural substances and a discussion of their origin, passing to a study of type operations, such as combustion, decomposition, solution, crystallization, precipitation, and fermentation, and ending the course with a study of the arts "which require some particular development in the local region where a school is situated."

Social arts, political economy, and commerce will also be taught, the instructor in these subjects also being charged with the teaching of grammar and the development of the ability to express oneself clearly and precisely in writing.

Elementary education for girls includes training in the arts of needlework, spinning, knitting, cooking, household management, care of the sick, physical education of the young, moral principles, history, local geography, and good taste and grace.

The preservation and defense of the nation and its commercial and industrial prosperity depend upon the learned professions, such as engineering, medicine, pharmacy, etc.; hence the proposal to establish institutes and *lycées* for the spread of the elementary knowledge required by these professions.

Industrial and agricultural prosperity are based not upon the brute strength of the workers, but on the intelligent use of machines and labor-saving devices. Agriculture is the key to all industry, since the other arts only process what agriculture produces. France, if she is wise, can triple her agricultural produce and become a mighty state. The proper marshalling of mechanical methods to this end should be a part of public education.

Research by scientist and artisan will add to our knowledge.[4] These men, therefore, should be independent and free. Society should assure them their subsistence. Such men should not have to teach for a living, but be free to invent and publish.

Progress in one of the sciences and arts being related to that of the others, there should be collaboration of all scientists: What would experimental physics and chemistry be if geometry had not introduced its methods there, its strictness in its manner of reasoning and its calculations? For this reason there should be common assemblies of scientists and artisans to "encompass even those knowledges which seem to have between them the least similarity or connection." Lavoisier continues:

> Representative citizens, the fate of the French Republic is in your hands; it is up to you to elevate France to the highest degree of splendor and prosperity . . . organize public instruction . . . give impulse to the arts, sciences, industries, and commerce. See with what ardor all nations, our rivals, busy themselves with the means of supplying, by industry, that which they lack in

[3] This is a sound principle and was earlier put to use by one of the most eminent figures in European education, John Amos Comenius (seventeenth century).

[4] Lavoisier was in reality here proposing the modern research institutes and the joint scientific and industrial societies and conferences of present times.

strength. . . . A nation in which the scientist and artisan languish in a state of stagnation would soon be outrun by rival nations . . . and become the prey of those who plan to invade it . . . . China serves as a lesson; their arts are what they were 2000 years ago, because their form of government has enchained the . . . sciences. Legislators—instruction has made the revolution . . . make use of the torch . . . in your hands. It is in this spirit that the plan . . . has been written.

We see three main influences in Lavoisier's philosophy: Locke's psychological basis for education, Rousseau's "nature-as-the-great-teacher," and Condorcet's tenet that "public education is a duty that society owes to all its citizens." With the latter, he holds that education should be organized as a function of the state and should concern itself with preparations for good citizenship. He works out his program of studies in far greater detail than did Condorcet, and because he recognizes, as did his great contemporary, that there are differences in native abilities and interests he asks for a new type of school—the vocational school, at the higher level—adding that such schools are needed for a class ignored until that time. He gives a detailed program for this kind of education. In making this proposal, Lavoisier was so far ahead of his time (as he so often was) that although efforts to establish courses in technical training have been made, it cannot be said, even at this late date, that his ideas have yet been realized in their entirety in French education. He pleads for extensive education in the sciences, both for the sake of training in the pure sciences and as a basis for the arts. With Condorcet he advocates education beyond the years of childhood and youth, and feels that science is the best of all educational areas.

Lavoisier (as did Condorcet before him) proposes the creation of a system which embraces four types of schools:

(1) The primary school, open to all children without distinction or exception, on attaining the age of six years, one school per 1000 individuals.

(2) The elementary schools of the arts and social economy, open to children at the age of eleven years, and located in the chief city of each district.

(3) The institute, or elementary school of sciences and arts (present-day French secondary schools and colleges), in the chief city of each *département.*

(4) The *lycée* or school of sciences and arts (present-day French university departments), twelve of which are to be located throughout the territory of the Republic.

In addition, he proposes a central society of sciences and arts which, among other duties, will constitute a jury for the purpose of encouraging and rewarding worthy contributions to the arts and sciences.

PRIMARY SCHOOL

He makes practical suggestions to the teacher: The methods, materials, and speed of progress should be adjusted to the order of development of the organs of the human body and the abilities of the child. Loss of attention can be prevented by taking care not to occupy children too long with one type of study. (What a practical psychologist he was!) In the early years it is wise to let learning take place in association with play, interest, and enjoyment, *i. e.*, through the senses. These are currently accepted psychological practices. The "three R's" are to mingle with natural history, historical stories, deeds of patriotism and charity, and trips to farm and industry, all taught principally in the form of games. Emphasis is upon the useful and the practical. Later, elementary principles of morals (ethics) are brought in: rights and duties of man, social, political, and commercial organization, bookkeeping, the use of a dictionary and a table of contents, understanding drawings, and community singing. This rudimentary education, although given separately, is the same for both sexes. (Unlike his great contemporary, he does not favor coeducation.)

For boys emphasis is placed upon the study of the elements of rural economy: farming, tree pruning, training of oxen and horses, iron-working and wagon-making, use of firearms, and swimming. The girls will be taught household arts. There is to be much representation by picture so that children may better understand the ideas being taught from the books, which will be written for them in the best possible manner, with stress upon the principles of liberty, equality, justice, charity, purity of habits, and patriotism. Books are to be so constructed that parts may be replaced with little trouble when torn, used, or lost. (An early version of our loose-leaf note-book?) In town schools the books will emphasize things relating to the arts and business, replacing the emphasis upon agriculture in the country schools.

Students will be organized into miniature models of republican society, so that they will learn sane ideas of order and justice. Infringement of rules is to be punished by the teacher only after judgment by a jury chosen from among the children.[5]

ELEMENTARY SCHOOL

In this school boys will be taught drawing, geometry, principles of machines, elements of natural history, physics and chemistry as applied to the arts and social needs, political economy, trade, double-entry bookkeeping, French constitution and law, how contracts are made and legalized, laws of inheritance, grammar, and composition. The girls will be taught drawing, household arts, ethics, history, local geography, physics, and chemistry. Teachers will hold Sunday and winter-evening meetings on arts and on morals (ethics) for people of all ages. Twice a year they will hold a general assembly at which the public will pass judgment on pupil progress. (To describe these activities today we would use the terms "public relations" and "evaluation.")

No one is denied the legal right to operate or attend a private school, but such students are required to register with the government for purposes of health examinations and certain personal information.

[5] This is an element of modern student government.

INSTITUTES

These will teach four disciplines, namely, languages, literature, and fine arts; ethical and political studies; mathematics and physical sciences; and arts and applied sciences. Equipment will include a library, physical apparatus, machine models, astronomical instruments, art supplies, and a botanical garden. A general council of the faculty will hold public meetings at which learned papers will be read. Paris will have five institutes, because of its size; other localities will have a proportionate number.

LYCÉES

These, like the institutes, will teach the four disciplines mentioned above and be similarly equipped. A council of the faculty will perform the same function as that of the institute. The *lycée* at Paris will be known as the Lycée National and comprise six branches or museums. One, located at the Bibliothèque Nationale, will teach ancient and modern languages, *belles-lettres*, the art of thinking, ethics, moral and political studies, history, geography, and antiquities. A second at the Louvre will teach the fine arts. A third at the Collège des Quatre Nations will be concerned with mathematical and physical sciences and serve as a museum for exhibition and demonstration of mechanical inventions. A fourth at the Observatoire de la République will be for astronomical teaching and observation. The fifth, at the Jardin des Plantes, for biological sciences and geology, will be renamed the Museum of Natural History. The sixth, known as the École de la Chirurgie, will teach veterinary and human medicine, including midwifery and pharmacy.

There will be a National Society of Sciences and Arts, consisting of the most distinguished members of the professions, for the advancement of learning in their fields and for communication with foreign learned societies, so as to enrich the Republic with the benefits of discoveries in the arts and sciences. The Society will have four divisions, each organized in smaller subdivisions for specialized fields. From among the members of the National Society a board will be established for distributing awards and pensions for distinguished scientific and artistic contributions.

INFLUENCE OF LAVOISIER'S PLAN

Lavoisier's detailed and comprehensive proposals for educational reform eventually exerted a considerable influence upon the decades to come. Based though they were upon the thoughts of Rousseau, Talleyrand, Condorcet, and others, they nonetheless presented such a clear and concise synthesis of earlier plans as to make his achievement creative. It is difficult to prove that present educational laws are the direct outgrowth of Lavoisier's plans alone, yet it seems clear that the following, among the principal laws of public education in France, are to be noted, in embryonic form, in his suggestions:

(1) The establishment of four grades of instruction (Talleyrand, Condorcet, Lavoisier).

(2) Freedom in teaching—Guizot's law of June 16, 1833 (Condorcet, Lavoisier).

(3) The establishment of girls' schools—Duruy's law, April 10, 1867 (Condorcet and, in embryo, in Lavoisier's work).

(4) Free education—Jules Ferry's law of June 16, 1881 (Talleyrand, Condorcet, and, in embryo, in Lavoisier's work).

(5) Compulsory education—Jules Ferry's law of March 28, 1882 (Lanthenas' plan of December 18, 1792, not exactly mentioned, but understood in Lavoisier's work).

(6) General organization of primary teaching; lay education (as distinguished from that of the church)—laws of Jean Macé and Paul Bert, October 30, 1886 (Condorcet, Lavoisier).

Reforms subsequent to the passage of these and other fundamental laws represent no radical departure from the basic structure of the system he proposed.

Lavoisier also helped plan an elaborate system of higher education and a college of national and international scope at Richmond, Virginia. A college building was actually erected in that city, but the college never got started, probably because of conditions in revolutionary France at that time.

Even though he knew from the numerous humiliations, denial of honors, and sabotage of his work, all at the hands of the agents of the Revolution during the years 1792–93, that the shadow of the guillotine was lengthening in his direction, he yet could give attention to the preparation of his "Reflections on Public Instruction." What eloquent testimony of the deep love which his tender and gentle heart held for little children, and indeed, for all mankind!

We of the twentieth century recognize the wisdom displayed in the passage quoted above. This plea for an education worthy of a free people, in whose future he hopes and believes so strongly, exhibits the spirit of a larger patriotism so frequently unnoticed and unsung. In a paraphrase of Lamartine we might say that, when he wrote, it was with thoughts of France; when he hoped, it was with love for France.

ACKNOWLEDGMENTS

The author wishes to acknowledge the help of the following: the Ministry of Education of France, for data on French educational laws; Fred Shulik, Malcolm Ecker, and Noel Kramer, students at Central High School, Philadelphia, Pennsylvania, and Mrs. Bella Heiman of Philadelphia, Pennsylvania, for assistance with the French translation; Denis I. Duveen and Herbert S. Klickstein, "A Bibliography of the Works of Antoine Laurent Lavoisier" (1743–94), in press.

A KINETIC INTERPRETATION OF THE BOUGUER-BEER LAW

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THE usual presentation of the Bouguer-Beer (or Lambert-Beer) law in elementary texts devotes little attention to the details of the process of light absorption. Likewise no convincing physical interpretation is normally given of the important parameter of the process, the so-called absorbancy index (or extinction coefficient). Liebhafsky and Pfeiffer[1] have recently given an excellent derivation of the law in more general terms than normal. For the beginning students in analytical or physical chemistry courses, however, a simple kinetic picture remedies the above-mentioned defects.

An incident beam of monochromatic light of intensity I impinges on a length b of solution containing c molecules per cubic centimeter. It is desired to derive an expression for the intensity I of the emergent beam as a function of c and b. For monochromatic light I is proportional to N, the number of photons striking a one square centimeter surface per second. We may ask then for the decrease, $-dN$, in the latter quantity after the light passes through a layer of solution db in thickness. The absorption of one photon by a molecule requires a "collision" or encounter of the two. Accordingly, the number of photons absorbed per second is proportional to the total number of collisions:

$$-dN = kcN\,db \tag{1}$$

or

$$\frac{-dN}{N} = kc\,db \tag{2}$$

Here k, the constant of proportionality, can be interpreted as the probability that a collision will lead to absorption. The quantity $c\,db$ gives the number of molecules in a segment of solution of unit cross section and db centimeters thick. The product $Nc\,db$ measures the number of collisions per second. In kinetic terminology the process is said to be first order in photons and molecules.

Since I is proportional to N, equation (2) is equivalent to

$$\frac{-dI}{I} = kc\,db \tag{3}$$

Integration yields the usual form of the Bouguer-Beer law

$$\frac{I}{I_0} = e^{-kcb} \tag{4}$$

This approach avoids separate derivations of the laws of Bouguer and Beer which are so frequently encountered in textbook treatments of the subject. Methods used to combine the two laws are frequently confusing to the student.

An interpretation of the constant k is best approached from the standpoint of dimensionality. Since the quantity kcb must be dimensionless, it is necessary that k have the dimensions of $1/cb$, *i. e.*, of area per molecule. This suggests then that k be identified as the effective "collision cross section" presented by one molecule to a photon of the given frequency. (The term "cross section" is quite commonly used in nuclear physics to describe the absorption by nuclei of various bombarding particles.) The dimensionless exponent, kcb (absorbancy or optical density), may be identified as the fraction of the unit cross-sectional area presented to the incident light beam which is occupied by photon-absorbing surfaces in the segment of solution. Thus it is easy to see that the fractional decrease in light intensity produced by passage through a layer db thick is equal to $kc\,db$, which may be recognized as the usual starting point in "deriving" the Bouguer-Beer law. Equation (4) is commonly written as

$$\frac{I}{I_0} = 10^{-a_m bc} \tag{4a}$$

Here c is the concentration in moles per liter and a_m is the molar absorbancy index (or molar extinction coefficient, ϵ).

The spectral properties of a solution are normally presented graphically as a plot of a_m (usually log a_m) against the frequency or wave length of the radiation. Ideally this curve is sharply peaked at the absorption frequencies and falls away rapidly above and below the maximum. The finite width of the peak reflects the fact that molecules absorb radiation over a wide range around the absorption maximum. According to the uncertainty principle this arises from the fact that the two energy levels involved in the transition induced by photon absorption are themselves correspondingly broad rather than sharp. Maximum probability for transition occurs at or near the center of the band.

This characteristic dependence of a_m upon wave length can be easily explained to beginners, however, by an analogy drawn from baseball. A shortstop's efficiency in converting groundballs into putouts at first base may be defined in terms of a "cross section"—the segment of the infield within which a given shortstop can convert hits into putouts. This cross section de-

[1] LIEBHAFSKY, H. A., AND H. G. PFEIFFER, J. CHEM. EDUC., 30, 450 (1953).

pends upon the speed of the ball, however. If the speed is too great the ball is through the infield before the shortstop reaches it, and if too slow, he cannot reach it in time to make the play at first base. Obviously, at some intermediate speed maximum efficiency is attained.

There are, of course, many situations in which deviations from the Bouguer-Beer law occur. An extension of the present picture might be useful in explaining such deviations. However, our purpose here is merely to present a simple derivation of the law under ideal conditions in an attempt to give beginners a more meaningful picture than usual of the process of light absorption.

<◊>

EXPERIMENTS MOST OFTEN REQUIRED IN COLLEGE GENERAL CHEMISTRY

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Two years ago a research project was conducted to find out what experiments are required for general chemistry courses in American colleges and universities. The purpose of the research was to arrive at a basic series of exercises widely applicable. An inquiry was sent to land-grant colleges and universities, state universities, private schools, and a select list of chemistry laboratory instructors. One hundred and twenty-nine forms were returned completed. One hundred and seven of these were used. They represented 94 schools and 39 states. The information sheet gave the names of manuals; the publisher and date; experiments required; method used (macro or semimicro); name of experiments used which were not listed in the manual or the syllabus; and curricula in which students are enrolled who are required to have only one year of chemistry. These manuals were obtained from publishers and by contributions from laboratory instructors. They were examined for titles of experiments required and tallied according to titles.

The following results were noted: (1) there were 150 experiments listed as used; (2) no one experiment was used by 100 per cent of the schools; (3) the percentages ranged from one to 86 per cent; (4) there was one experiment required by 86 per cent of the schools; and (5) 18 experiments were used once. The table presents the majority of experiments used by the schools represented.

Experiments Most Often Used

Titles	*% of schools using experiments*
(1) Equivalent weight	86
(2) Titration	81
(3) Chemistry of nitrogen and its compounds	77
(4) Simple oxidation-reduction	72
(5) Molecular weight of a gas	72
(6) Hydrogen—preparation and properties	70
(7) Physical and chemical properties	70
(8) The halogens and their important compounds	69
(9) Some properties of acids and bases	67
(10) Chemical equilibrium	63
(11) Determination of a formula from experimental data	63
(12) Water—its physical and chemical properties	62
(13) Sulfur and its important compounds	62
(14) Introductory laboratory techniques	57
(15) Concentration of solutions	57
(16) Ionic reactions	56
(17) Oxygen—preparation and properties	56
(18) Laws of Boyle and Charles	56
(19) Hydrolysis	52

In so far as this study may be indicative, it seems reasonable to conclude (1) that few experiments are widely used, but those listed are basic in establishing principles of chemistry and concomitant learning; (2) that not many experiments were required that relate directly to the everyday life of the student; (3) that a definite trend toward general inorganic chemistry rather than general chemistry was apparent, since 30 of the 94 schools offer qualitative analysis in the first year of chemistry, and this trend is further substantiated by the few experiments required in organic chemistry; (4) that there is a definite tendency to use semimicro technique in preference to macro technique, 28 per cent of the returns indicating the use of the former for general chemistry; (5) that there were 61 different manuals used by the 94 schools (as few as nine schools used the same manual); (6) that nearly all of the manuals rated high in procedures entailing fundamental laws, concepts, theories, in serving as suitable background for advanced scientific work, and establishing basic laboratory techniques; (7) that the manuals did not rank as high in the use of the scientific method and in the interpretation of everyday phenomena; and (8) that more space was given to deductive procedure than to the inductive method.

CLARA MARIE DEMILT (1891–1953)[1]

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When an attack of coronary thrombosis struck Dr. Clara deMilt on Sunday morning, May 10, 1953, an end was brought to the fruitful life of a colorful person. She was at the peak of her activity in the history of chemistry and left many projects unfinished, but in the preceding years her enthusiasm and zeal for the historical approach to science had inspired many of her students and had borne fruit in articles published by her former students.

Clara Marie deMilt was born on the 8th of May, 1891, in New Orleans; she attended the public schools in Biloxi, Mississippi, and entered H. Sophie Newcomb College in September, 1907. In college she took courses in chemistry while majoring in English and history; she received the B.A. degree in 1911 and was elected to Phi Beta Kappa. After graduation she taught in the high schools of Jefferson Parish until 1919. She then entered Tulane University Graduate School and in 1921 received the degree of Master of Science in Chemistry. At this time she began her teaching career as an instructor in chemistry at Newcomb and taught there continuously until her death, excepting only the year she was on leave to complete her graduate work at the University of Chicago, where she was awarded the doctorate in 1925.

Dr. deMilt became Assistant Professor of Chemistry in 1925, was advanced to Associate Professor in 1927, was made Head of the Department in 1926 and Professor in 1930. In 1941 she became Chairman of the Chemistry Department of the Graduate School of Tulane University, serving in that capacity until 1949, when she resigned in order to devote more time to writing. During this period, which witnessed the expansion of graduate work and the first Ph.D. in chemistry, she guided many graduate students in planning their work. Her boundless enthusiasm for chemistry, along with her sincere interest in people, inspired the confidence of those seeking her advice. Many of the young women who majored in chemistry under her tutelage at Newcomb have gone on to successful careers in chemistry, medicine, and pharmacology.

Dr. deMilt was active in research in organic chemistry, and directed graduate students in their research in that field. There seems to be no doubt that her interest and activity in history of chemistry stemmed from her literature research and early training in history and English. She will be remembered best for her years of work in building up a library for research in the history of chemistry at Tulane, as well as for her own activity in the field. Her graduate courses in the history of science and chemistry were unusual; her lectures always made the men, the periods, and the chemistry live again in the classroom. Papers by her students in THIS JOURNAL are testimonials to her enthusiasm and zeal for the subject. Dr. deMilt did not permit the use of her name as a co-author although she advised and helped the students with their papers; she preferred only a statement of appreciation at the end of the article.[2]

Dr. deMilt's studies of the lives of some of the men who made chemistry are characterized by thorough investigations; in several instances she found evidence to prove that men had received priority when others should have been credited for the work. She was the first to point out the fact that Robert Hooke's ideas on combustion preceded those of Dr. John Mayhow;[3] again, she proved that Nicolas Lemery had copied most of his famous "Cours de Chymie" (1677) from "Traité de la Chymie" (1668) written by Christopher Glaser.[4] Dr. deMilt was an authority on the work of chemists in the seventeenth and eighteenth centuries, but later when she began collecting material for her manuscript (unpublished) on the history of organic chemistry she became interested in nineteenth-century chemists. Her studies revealed that Charles Gerhardt could not have written his great treatise on organic chemistry had he not taken most of his ideas from Auguste Laurent while working in the latter's laboratory.[5]

Dr. deMilt brought enthusiasm and zest into her teaching; her lectures were given in her own inimitable manner and one could not help being impressed with her love for chemistry and its history. She seemed to live and breathe the subject matter, and her interest never lagged. Her personality was characterized by sincerity, honesty, and direct forthrightness; her colleagues were always sure about her opinions and feelings, for she was never hesitant in expression of her views. Although her physical capacity for hard work declined in the last two years, she continued to drive herself in an effort to complete a "History of Organic Chemistry." She must have had some premonition of an early death; when the author said she was working

[1] Presented before the Division of History of Chemistry at the 125th Meeting of the American Chemical Society, Kansas City, March, 1954.

[2] This fact has made it extremely difficult for the author to be sure he has located all of the papers inspired by her teaching.

[3] DEMILT, C., "Robert Hooke, chemist," J. CHEM. EDUC., 16, 503 (1939).

[4] DEMILT, C., "Christopher Glaser," *ibid.*, 19, 53 (1942).

[5] "Auguste Laurent—guide and inspiration of Gerhardt," *ibid.*, 28, 198–204 (1951).

too hard, her comment was, "But I must, there are so many things left I want to finish." Although suffering from arteriosclerosis, which she called "gout," she continued to drive herself up to the last.

Along with her love of chemistry came her vacation tours of the country by auto. Accompanied by her friend and companion, Miss Amy Taggart, she would leave New Orleans in June and return in September. These vacation tours were not just for travel—books and notes went along; trips were planned so that more or less lengthy stops could be made at libraries to locate historical material. Dr. deMilt was familiar with nearly all of the University libraries in the United States and knew just where to find historical material. Upon her return the car would be loaded with a collection of rocks, and she would be enthusiastic about the location of more historical data. A part of her rocks, carefully identified, form part of a collection in several cabinets near the chemistry laboratories in Newcomb Hall; the others are in a rock garden at her home. Some of her stories of travel over unimproved roads through the mountains to and from the west coast caused the author to wonder how two women could lead such charmed lives.

While Clara deMilt was devoted to teaching and the history of chemistry, she always did more than her share of the usual faculty committee work, primarily because she always worked on and thought about every assignment. She was a life member of the New Orleans Academy of Science and an active member of the Louisiana Section of the American Chemical Society. She served on the Program Committee of the Section for many years and was elected Councilor for 1943–47, but declined the nomination for Chairman because of the time it would take from her writing. The Tulane Chapter of Sigma Xi considered her as one of their most distinguished members.

A more fitting close to this paper cannot be made than to quote from the insert placed in *Chymia*, Vol. 4.

> Prof. deMilt brought to her studies in the history of chemistry an extraordinary zest and enthusiasm and had a rare talent for communicating that enthusiasm to others... It is a source of gratification to us that this volume contains one of the last papers from her pen.[6]

A list of her publications and those by others under her guidance follows.

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(1) (with B. H. Nicolet) "Phenylacetic acid from oleic acid," *J. Am. Chem. Soc.*, **49**, 1103 (1927).
(2) ——and G. Van Zandt, "Diazotization of weakly basic amines," *ibid.*, **58**, 2044 (1936).
(3) "Robert Hooke, chemist," J. Chem. Educ., **16**, 503 (1939).
(4) ——and M. Sarton, "Preparation of 4,4′-dicyanobiphenyl and certain ketones of biphenyl," *J. Am. Chem. Soc.*, **62**, 1954 (1940).
(5) "Early chemistry at Le Jardin du Roi," J. Chem. Educ., **18**, 503 (1941).
(6) "Christopher Glaser," *ibid.*, **19**, 53 (1942).
(7) "Karl Weltzien and the congress at Karlsruhe," *Chymia*, **1**, 153 (1948).
(8) "The value of the historical approach in the teaching of general chemistry," J. Chem. Educ., **26**, 39 (1949).
(9) "Auguste Laurent—guide and inspiration of Gerhardt," *ibid.*, **28**, 198 (1951).
(10) "The value of the history and philosophy of science in the training of graduate students in chemistry," *ibid.*, **29**, 340 (1952).
(11) "Auguste Laurent, founder of modern organic chemistry," *Chymia*, **4**, 85 (1953).
(12) ——and Charlotte H. Boatner, "A Laboratory Manual of Organic Chemistry," Edwards Bros., Ann Arbor, Michigan, **1934**, **1938**.
(13) ——and Elsie G. Ferguson, "A Laboratory Manual of General Chemistry," Edwards Bros., Ann Arbor, Michigan, **1938**, **1939**; ——and Anna J. Harrison, *ibid.*, **1941**, **1945**; ——and Virginia F. McConnell, *ibid.*, **1952**.

PUBLICATIONS BY OTHER AUTHORS

(1) Boatner, Charlotte H., "Certain unpublished letters from French scientists of revolutionary period taken from the files of Joseph Lakanal," *Osiris*, **1**, 173 (1936).
(2) Raulins, Rebecca, "The Beckmann rearrangement of certain furyl ketoximes," *Proc. Louisiana Acad. Sci.*, **4**, 457 (1938).
(3) Ferguson, Elsie G., "Bergman, Kloproth, Vauquelin, Wollaston," J. Chem. Educ., **17**, 555 (1940); **18**, 3 (1941).
(4) Kapp, Mary E., "Some early American students of chemistry at the University of Edinburgh, 1750–1800," *ibid.*, **18**, 553 (1941).
(5) Cameron, Margaret D., "Victor Meyer and the thiophene compounds," *ibid.*, **26**, 521 (1949).
(6) Schmidt, Gustav, "The discovery of the nitroparaffins by Victor Meyer," *ibid.*, **27**, 557 (1950).
(7) Carter, Mary K., "The history of barbituric acid," *ibid.*, **28**, 524 (1951).
(8) Ruckstuhl, Annette, "Thomas Graham's study of the diffusion of gases," *ibid.*, **28**, 294 (1951).
(9) Alsobrook, Jane W., "Jean Baptiste André Dumas," *ibid.*, **28**, 630 (1951).
(10) Sistrunk, Thomas O., "John Frederic Daniell," *ibid.*, **29**, 26 (1952).
(11) Zietz, Jr., Joseph R., " 'The Pirotechnia' of Vannoccio Biringuccio," *ibid.*, **29**, 507 (1952).
(12) Roussel, Philip A., "The Fischer indole synthesis," *ibid.*, **30**, 122 (1953).
(13) Russell, Justin, "Edmund Davy," *ibid.*, **30**, 302 (1953).
(14) McConnell, Virginia F., "Hlasiwetz and Barth—pioneers in the structural aspects of plant products," *ibid.*, **30**, 380 (1953).

[6] "Auguste Laurent, founder of modern organic chemistry," *Chymia*, **4**, 85 (1953).

SUBLIMATION CURVE, VAPORIZATION CURVE, AND TRIPLE POINT DETERMINATION[1]

An Undergraduate Experiment

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THE determination of the vapor-pressure curve of a pure liquid by the Ramsay and Young method (measurement of the boiling point under various pressures) is a familiar experiment in the undergraduate curriculum in physical chemistry. That the method is also applicable, with some modification, to the sublimation curve of an appreciably volatile solid seems to have been largely overlooked, perhaps because it appears doubtful that equilibrium between solid and vapor will be reached readily. Strangely enough, equilibrium is often readily attainable, as Ramsay and Young[2] themselves showed for several solids, and the writers have found that their technique can be modified and simplified to give an experiment suitable for the standard laboratory course in physical chemistry. It permits the measurement of the sublimation pressure of a solid, followed without interruption by that of the vapor pressure of its liquid. The resulting data lead immediately to location of the triple point temperature and pressure and thence to the unary phase diagram. The time required for assembling the apparatus and making the measurements is not more than two hours.

Solids with appreciable sublimation pressures at easily accessible temperatures are not common, but at least half a dozen have been found feasible in the experiment to be described. The one recommended is salicylic acid: its triple point is conveniently located, it equilibrates quickly, it is nonhazardous and inexpensive, and it allows easy cleaning afterward.

The apparatus is shown in Figure 1. The powdered solid *A* is placed in a container made by removing the bulb and side arm from a 500-ml. Claisen flask. Sufficient solid is used so that, when molten, it will fill only the portion of the vessel below the crotch, and yet, when solid, will cover the bulb of the thermometer *B* completely. The air condenser *C* leads to a tank or carboy *D* (for a buffer against pressure changes) and thence to a manometer, three-way stopcock *E*, air-leak, and pump. (A Hyvac is necessary for work with salicylic acid but a water aspirator can be used with certain other substances.) For salicylic acid a 0–260° thermometer and the standard portable type of manometer (0–44 cm.) are adequate, although a manometer covering a wider range increases the range of measurements.

When assembled, the apparatus containing the solid is evacuated to a few millimeters and the pump connection turned off. The solid is heated gently by brushing with a free flame. The temperature rises and reaches a constant value at the temperature for which the sublimation pressure equals the pressure given by the manometer. Happily, the solid condenses in an adherent coating on the thermometer bulb so that the procedure adopted by previous workers,[2] of coating the bulb by dipping it repeatedly into the molten material, is quite unnecessary. The temperature and pressure are recorded and a small amount of air allowed to leak in to raise the pressure by 2 or 3 mm. The solid is now heated further until a new constant temperature is reached and again temperature and pressure are

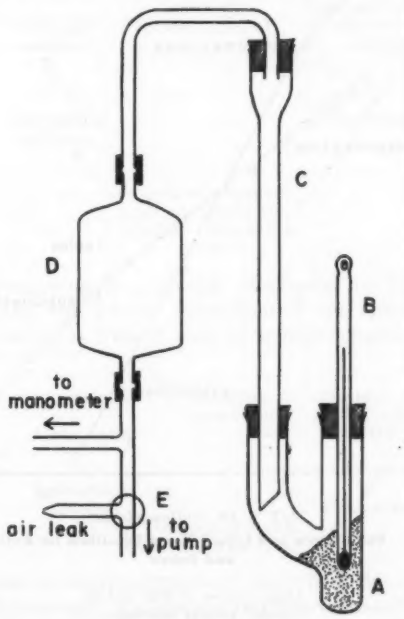

Figure 1. Apparatus

[1] Presented before the Meeting-in-Miniature of the New York Section of the American Chemical Society, February, 1954.

[2] RAMSAY, W., AND S. YOUNG, *Trans. Roy. Soc. London*, **A175**, 37 (1884); *J. Chem. Soc.*, **47**, 42 (1885); **49**, 453 (1886); see also LINDER, E. G., *J. Phys. Chem.*, **35**, 531 (1931).

recorded. This procedure is continued until, when the pressure reaches about 20 mm. and the temperature about 160°, the solid melts and exposes the bulb completely. The technique is unaltered by melting, however, for pressures are increased (by gradually increasing amounts) and the corresponding constant temperatures (boiling points) observed as before. The normal boiling point of salicylic acid, 256°, is easily accessible, although the temperature range cannot be extended beyond 230° with a manometer limited to pressures under 44 cm. In any case, the acid gradually decomposes with rise in temperature with a corresponding increased error in measurement. The resulting data are now plotted (log p versus $1/T$), giving two nearly straight lines, the intersection of which locates the pressure and temperature of the triple point, and the slopes of which lead to calculation of heats of sublimation, vaporization, and fusion. Figure 2 gives the results of typical runs with iodine and anthraquinone and includes literature values quoted by Stull.[3] The data on a p-t diagram, with the addition of a fusion curve (vertical straight line), yield the phase diagram immediately.

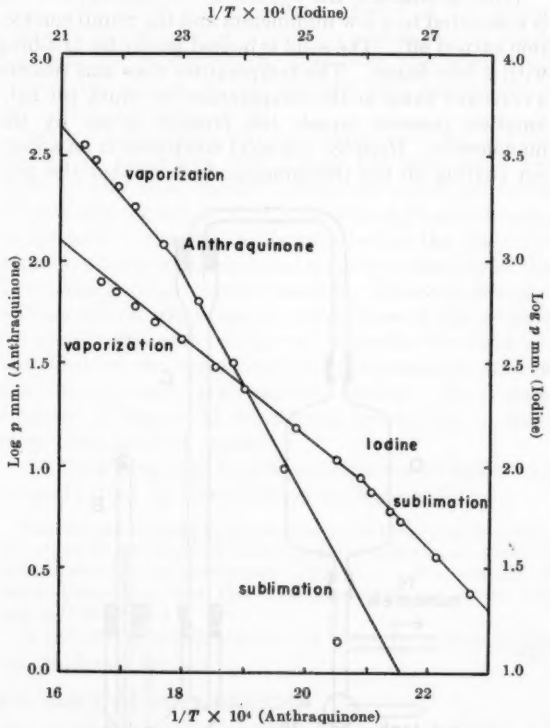

Figure 2. Solid-Vapor and Liquid-Vapor Equilibria for Anthraquinone and Iodine

Lines: values of Stull (ref. 3).
Circles: present technique.

Although salicylic acid is water-soluble, ethanol will be found better for cleaning the apparatus, and at least 20 minutes should be allowed the student for this purpose.

Figure 3. Apparatus Modified for Rapidly Subliming Solids

Substances to which the above technique has been found applicable are salicylic acid, hexachlorobenzene, iodine, hexachloroethane, camphor, anthracene, and anthraquinone. U. S. P. grade chemicals are satisfactory. For one reason or another, all but the first two listed are less appropriate for student use. Iodine gives excellent results but is, of course, obnoxious. Camphor requires too careful heat regulation. Both are removed from the apparatus with difficulty but have an advantage in that a water aspirator can be substituted for the Hyvac. Hexachloroethane works well but gives only the sublimation curve. Anthracene and anthraquinone volatilize so rapidly, even though their vapor pressure is lower than that of all the other substances mentioned, that a portion of an 18-mm. test tube, tapered at its open end, must be used to jacket the thermometer bulb and contain the solid, as in Figure 3. A convenient summary of literature values for sublimation and vapor pressure will be found in Stull's compilation,[3] although we question the data given there for hexachlorobenzene.[4]

It should be pointed out, in conclusion, that the above technique is not applicable to all volatile solids: it is feasible only when their sublimation pressures are sufficiently large and when they equilibrate readily.

[3] STULL, D. R., *Ind. Eng. Chem.*, **39**, 517 (1947).

[4] See, however, SEARS, G. W., AND E. R. HOPKE, *J. Am. Chem. Soc.*, **71**, 1632 (1949).

PARTITION CHROMATOGRAPHY, AN ISENTROPIC SEPARATION PROCESS

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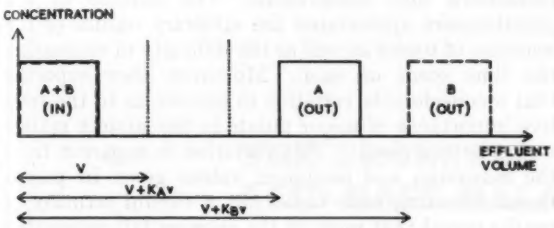
THE result of a partition-chromatographic separation under ideal conditions may be expressed in a diagram showing concentrations against effluent volume, as follows:



The solvent originally associated with the solutes will appear after a volume V has passed through the column, V simply being the hold-up of moving phase in the column.

A solute will be retarded. If the volume of stagnant phase in the column is v and the partition coefficient over stagnant and moving phase is K, the volume v of stagnant phase is equivalent to a volume Kv of moving phase, *i. e.*, the solute will appear after a volume $V + Kv$ has passed.

By a suitable choice of solvents two components, A and B, may be given different K values and may thus be separated.

After the separation the column is back in its original state. We then have separated two solutes without doing any work. The friction in the column clearly has no influence because it is the same as would be observed for the pure solvent.

One is now tempted to conclude that the separation as described is a reversal of a diffusion process. Such diffusion, however, according to the second law of thermodynamics, should be irreversible. The purpose of this communication is to draw attention to this paradox and to give its solution.

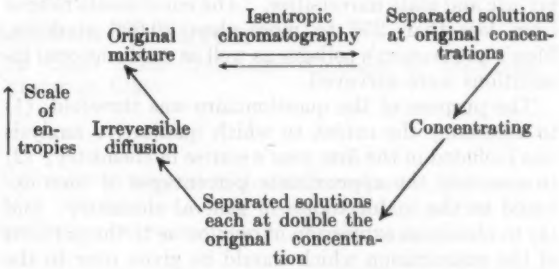
The process is indeed an isentropic process under the ideal conditions postulated, when a concentration profile does not change when passing through the column. These ideal conditions include immediate equilibrium, *i. e.*, an infinite number of ideal stages, so that all transfer takes place with an infinitely small driving force, *i. e.*, under reversible conditions. Also, other irreversibilities, such as diffusion and eddy diffusion, are assumed to be absent.

Indeed, the laws for the entropy of solutes in solution show the entropy in the mixed solution to be equal to the sum of the entropies in the separated solutions.

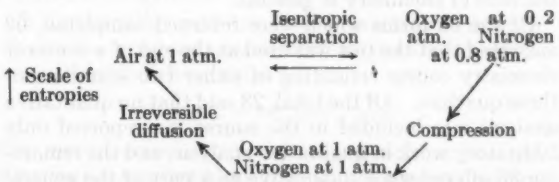
It is interesting to note that by feeding the separated solutions with an appropriate time lag to the same column, we may, again isentropically, restore the original state.

The solution of the paradox is that the process is *not* the reversal of a diffusion process. If we mix the separated solutions by diffusion the mixture has *double* the original volume. We must therefore concentrate the separated solutions, that is, decrease their entropies, before we can restore the original state by diffusion.

Thus,



This reasoning is perfectly analogous to the one used in the well known derivation of the entropy of gaseous mixtures with the aid of semipermeable membranes:



Students of thermodynamics often find the derivation of the entropy of a gaseous mixture rather difficult. Perhaps the impossibility of experimental realization of the membranes is partly responsible for this.

It should therefore be of interest that the separation of gases has its analogy in partition chromatography. It is true that ideal partition chromatography cannot be realized. However, in actual partition chromatography the result is so close to the ideal one, that the idealization of the concentration profiles, as shown in the figure, is considered acceptable without comment.

SOME TRENDS IN THE TEACHING OF GENERAL CHEMISTRY[1]

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At a meeting of the General Chemistry Subcommittee of the Committee on Examinations and Tests of the American Chemical Society, held in Atlantic City in September, 1952, it was decided that a survey of opinions of recent users of the general chemistry test would be helpful in formulating future examinations. Accordingly, with the help of Dr. T. A. Ashford, chairman of the committee, Dr. C. E. Ronneberg, chairman of the subcommittee, and Dr. Donald Wright, who had served as acting chairman of the subcommittee, a questionnaire was prepared and distributed to 150 institutions which had made use of the general chemistry test in the past year or two. These institutions represented a cross section of colleges and universities in the United States. Included were junior colleges, liberal arts colleges, state teachers' colleges, and private and state universities. The enrollments ranged from less than 250 to more than 20,000 students. Men's and women's colleges as well as coeducational institutions were surveyed.

The purpose of the questionnaire was threefold: (1) to determine the extent to which qualitative analysis was included in the first year's course in chemistry; (2) to ascertain the approximate percentages of time devoted to the major topics in general chemistry; and (3) to obtain an expression of opinion as to the portions of the examination which should be given over to the several types of questions.

A résumé of the results of the survey is here presented in the hope that it will interest not only users of the A. C. S. General Chemistry Examination but teachers of chemistry in general.

Of the 65 forms which were returned completed, 62 answered that the test was used at the end of a one-year chemistry course consisting of either two semesters or three quarters. Of the total, 23 said that no qualitative analysis was included in the course, six reported only laboratory work in qualitative analysis, and the remaining 36 offered some qualitative as a part of the general chemistry course. The average amount of time spent in class, including lecture and quiz–discussion periods, was 3.06 hours per week (range 2 to 4), while 3.49 hours per week were spent in the laboratory (range 0 to 6). There was some indication that the larger institutions offered more class time, averaging over $3^1/_4$ hours per week, as opposed to less than 3 hours per week for institutions of less than 5000 students. No correlation between size of college and time spent in laboratory was observed. More than three-quarters of the 25 institutions with enrollment below 1500 offered some qualitative in the first year, whereas only slightly more than half of the larger schools included qualitative.

In the portion of the questionnaire devoted to subject matter, the major topics were listed along with some breakdown into subdivisions. The authors of the questionnaire appreciated the arbitrary nature of the selection of topics as well as the difficulty of estimating the time spent on each. Moreover, they expected that a considerable variation in opinion as to the relative importance of major points in the subject matter would be expressed. This variation is apparent from the maximum and minimum values given in parentheses following each topic, yet a careful scrutiny of results reveal that most of the answers fall reasonably close to the averages. The topics are listed in order of their importance as indicated by the per cent of time spent on each in the course:

Nonmetals and their compounds	15.11%	(30–3)
Metals and their compounds	12.34	(30–0)
Chemical calculations	9.59	(20–3)
Atomic theory	8.23	(23–0)
Ionic theory	8.10	(20–0)
Fundamental definitions, symbols, formulas, equations, laws	7.02	(15–1)
Kinetic theory	5.96	(16–2)
Chemical equilibrium	5.52	(12–0)
Solutions	4.97	(14–2)
Qualitative separations	4.88	(25.5–0)
Oxidation and reduction	4.42	(15–0.5)
Periodic law	4.18	(20–0)
Organic chemistry	3.45	(10–0)
Electrochemistry	2.59	(10–0)
Colloids	1.38	(5–0)
Other topics	1.89	(20–0)

Eighteen of the schools reported no organic in the course. These included the three having less than a year's work. Strangely enough, more institutions giving no qualitative were in the no-organic group than were those which offered qualitative. Other topics receiving no time in the first year were colloids (14 institutions), electrochemistry (6), equilibrium (2), and atomic theory, periodic law, metallic elements, and ionization (one each).

An attempt to discover a relationship between time devoted to various topics and qualitative offerings revealed that such topics as ionization equilibrium, oxidation and reduction, and electrochemistry received more attention when qualitative analysis was included, while colloids, nonmetallic elements, and metallic elements received less.

In the last part the person answering was given a

[1] Presented at the General Chemistry Conference held at Pennsylvania State College, June 10–20, 1953.

chance to indicate the portion of examination time he felt should be devoted to the several types of questions. The last three topics, namely, organic chemistry, qualitative analysis, and chemistry of the metals, were appended to find out whether such material should be included in the main portion of the test or added as optional parts. The low percentage given to organic chemistry is undoubtedly an indication that few find any time to devote to that field in the first year. This is borne out by the small percentage of time (3.45 per cent) devoted to organic, as indicated above. The question on chemistry of the metals was put in as a result of several requests for more questions on the second semester's material.

The relative importance of question types was as follows:

General knowledge and information	22.5%
Quantitative application of principles	20.9
Qualitative application of principles	16.6
Scientific method	10.4
Chemistry of the metals	9.7
Laboratory technique	8.7
Qualitative analysis	6.0
Organic chemistry	4.3

The author wishes to take this opportunity to thank the members of the committee and those who took the time to answer the questionnaire for their generous cooperation.

THE BRÖNSTED THEORY APPLIED TO ACID-BASE BALANCE AND RESPIRATION[1]

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In previous reports,[2,3] the Brönsted concept of acids and bases was commended as an advance in chemistry that offers an excellent "tool" for explaining certain biological processes. The purpose of this paper is to point out that advantages can be gained by using this theory when explaining acid-base balance and respiration. The theory shows that there is a direct correlation between pH and acid-base balance. It clearly illustrates the equilibrium existing between acids, bases, and H ions of the various buffer pairs as indicated in the following equations:

acid	⇌	base	+	proton (hydrogen ion)
$H \cdot HCO_3$	⇌	HCO_3^-	+	H^+
$H \cdot HPO_4^-$	⇌	HPO_4^{--}	+	H^+
$H \cdot Pr$[4]	⇌	Pr^-	+	H^+
$H \cdot Org$[5]	⇌	Org^-	+	H^+

These acids and bases are important buffer pairs of the animal body. Excess hydrogen ions combine with the bases, thus preventing a rapid decrease in the pH of the solution, while the acids furnish hydrogen ions to prevent a rise in pH. It should be understood that H ions are combined with water and actually exist as H_3O^+ (hydronium) ions. One could illustrate the equilibrium between the acid and the base as:

$$\underset{\text{acid}}{H \cdot A} + H_2O \rightleftarrows \underset{\text{base}}{A^-} + \underset{\text{hydronium ion}}{H_3O^+}$$

This is not necessary because it is logical to assume that all ions are hydrated in H_2O solutions.

To further illustrate the direct correlation between pH and the acid-base equilibrium one can use the Henderson-Hasselbalch equation:

$$pH = pK_a + \log [\text{base}]/[\text{acid}]$$

This mathematical expression indicates that the pH of a solution is affected by the ratio of base concentration to the acid concentration. As *one would expect,* an increase in base-to-acid ratio increases the pH and a decrease in base-to-acid ratio decreases the pH of the solution.

What then is the function of the cations (Na^+, K^+, etc.) in acid-base balance? It is not difficult to answer this question, because where anions occur, there must be an equivalent amount of cations. Therefore the cations must be present as "companions" for the basic anions. With a loss of such cations, there will be a decrease in pH if there is a decrease of the base concen-

[1] Presented before the Division of Biological Chemistry at the 124th Meeting of the American Chemical Society, Chicago, September, 1953.
[2] Devor, A. W., *Science,* **104,** 492 (1946).
[3] Devor, A. W., *Proc. S. Dakota Acad. Sci.,* **28,** 39–42 (1949).
[4] $H \cdot Pr$ = protein in acid form.
[5] $H \cdot Org$ = organic acid.

tration (HCO_3^-, for example) to such an extent that the base-to-acid ratio is decreased. The CO_2-combining capacity of the blood is sometimes called the "alkali reserve." When CO_2 is taken up by the blood, it forms H_2CO_3, which is neutralized by the basic anions (HPO_4^{--}, protein$^-$) yielding HCO_3^-, while the cations are present as "companions" to the bases.

The basic behavior of nitrogen bases (purines, pyrimidines, etc.) and the amphoteric behavior of amino acids and proteins fits into the picture because they function as proton (H ion) donors or acceptors, or both. It is unnecessary to think in terms of the hydrated molecules as is the case when one uses the Arrhenius theory. Likewise, the basic behavior of substances such as $NaHCO_3$ and Na_2HPO_4 can be easily understood without thinking of the hydrolyzed salts.

A Teaching Aid. Students of chemistry are now being taught to think of an acid as a proton donor and of a base as a proton acceptor. Therefore it seems that advantages would be gained if we used these ideas for the explanation of the acidic and basic behavior of biological materials. We should realize that chemical theories have changed considerably since the ideas of acids and bases were first introduced into our biochemistry texts. The Brönsted theory helps to avoid the confusion that is sometimes encountered when one tries to explain the basic properties of body fluids on the cation content. Instead, it makes possible a simple explanation as to why the cations have been called bases. Students find the theory very helpful in explaining the principles of respiration and the chloride shift. When the Henderson-Hasselbalch equation is applied, it is not difficult for students to understand that the base-to-acid ratio must not change if the pH is to remain constant. This approach to acid-base balance is very simple because as one adds base or removes acid, the solution tends to become more alkaline, while the addition of acid, or removal of base, tends to cause a more acidic solution.

The "Alkaline Tide." When HCl is produced by the parietal cells and secreted into the stomach, hydrogen ions are removed from the always available $H{\cdot}HCO_3$ (CO_2 and H_2O are always present) as illustrated in the following equation:

$$CO_2 + H_2O \rightleftharpoons H{\cdot}HCO_3 \rightleftharpoons HCO_3^- + H^+$$

The concentration of HCO_3^- of the blood is temporarily increased, and the urine may become more alkaline. However, most of this "alkaline tide" bicarbonate is soon secreted into the intestine where its function is to neutralize the HCl coming from the stomach, resulting in an over-all neutral action. In other words, the HCO_3^- formed during the production of gastric HCl is soon eliminated via the intestine.

Utilization of Acids and Bases. One of the first steps in utilization of amino acids for energy is the removal of the basic amino group to produce NH_3 and an organic acid. The liver prevents an accumulation of the strong base, NH_3, by converting it into the nearly neutral amides, urea and glutamine. Since these amides are weakly acid and weakly basic, they have very little effect upon the pH of the body fluids. Organic acids such as α-keto glutaric acid, acetic acid, oxaloacetic acid, citric acid, and pyruvic acid do *not* decrease the pH of the blood because they are utilized by the body through the Krebs cycle or converted to neutral compounds such as glycogen and neutral fats. When the Na or K salts of these organic acids are taken into the body, there will be a basic reaction because the negative ions of such salts accept H ions from $H{\cdot}HCO_3$ (see equation above) to form more HCO_3^- (alkali reserve) and an organic acid. Organic acids thus formed have a neutral action as described above. Therefore, many salts of organic acids will cause an alkaline urine while the acids themselves have a neutral action. This explains why fruits and vegetables cause an alkaline urine.

Function of the Kidneys in Acid-Base Balance. Acids like sulfuric and phosphoric acids are not utilized as are the organic acids mentioned above, and when they are produced in the body, the kidneys produce NH_3, which combines with the H ions of these strong acids, forming NH_4^+, which is immediately excreted. The negative "partners" for NH_4^+ are SO_4^{--}, $H_2PO_4^-$, HPO_4^{--}, and Cl^-. The HCO_3^- is thus spared along with its "partner," Na^+. If the kidney fails to produce NH_3 as needed, the H^+ concentration of the blood increases, and these excess H ions are in part taken up by the HCO_3^-, (see equation above) to form $H{\cdot}HCO_3$. The ratio of base to acid (HCO_3^- to $H{\cdot}HCO_3$) is then decreased and the pH of the blood falls as is illustrated by the Henderson-Hasselbalch equation.

Although the sodium ion is potentially a weak acid, one should remember that it is very important in acid-base balance, and it is often considered to be a base-forming element. When too much sodium is lost, HCO_3^- cannot be formed unless this Na^+ is replaced, because the Na^+ is the common or natural "companion" for HCO_3^- in the extracellular fluid. When the kidneys function normally, they can produce NH_3, which accepts H ions from $H{\cdot}HCO_3$, and the NH_4^+ may be excreted as NH_4Cl. Thus NaCl may act as a "base-former." However, it is the HCO_3^- formed which is responsible for the basic action, and it should be recognized as the base.

Acidosis. If organic acids enter the blood stream at a very rapid rate, uncompensated acidosis may occur. Such is probably the case of acidosis in a diabetic individual, where an excessive amount of acetoacetic and β-hydroxybutyric acids are formed. Upon examination of the blood during such a condition of acidosis, we find that the HCO_3^- concentration is comparatively low and that the base-to-acid ratio is below normal. This happens as the base (HCO_3^-, for example) accepts H ions from the stronger acids to form other acids ($H{\cdot}HCO_3$, for example).

In some cases of diarrhea there is considerable loss of HCO_3^- via the intestine. In addition, there may

be a starvation effect and the metabolic process will use body tissue, resulting in a release of acids which must be neutralized. The "alkali reserve" may be drawn upon when such acids are produced at a very rapid rate, causing a decrease in the base-to-acid ratio (HCO_3^- to $H \cdot HCO_3$, for example). These conditions can be better understood when illustrated by the Henderson-Hasselbalch equation.

Alkalosis. During excessive vomiting there will be a loss of H ions from the body. The body can produce more hydrogen ions from the "always available" CO_2 and H_2O as illustrated in the following equation:

$$CO_2 + H_2O \rightleftharpoons H \cdot HCO_3 \rightleftharpoons H^+ + HCO_3^-$$

However, excessive loss of H ions causes an increase in the base-to-acid ratio and the pH of the blood will then rise above 7.4. In such cases, uncompensated alkalosis results. When individuals with peptic ulcers take large amounts of alkalies, the hydrogen ions may be used up as they are secreted into the stomach. When this happens, the HCO_3^- concentration of the blood is then increased as in the cases of excessive vomiting.

During hyperventilation a comparatively large amount of CO_2 is lost and reserve $H \cdot HCO_3$ is then used to produce more CO_2. Although there is some decrease in HCO_3^-, the base-to-acid ratio increases, resulting in a rise in pH. This condition of alkalosis can be better understood by the aid of the Henderson-Hasselbalch equation.

Respiration and the Chloride Shift. The Brönsted concept is very helpful in explaining the CO_2-carrying capacity of the blood. As the blood is pumped through the lungs, O_2 diffuses into the erythrocytes and combines with the HHb (hemoglobin) to form $HHbO_2$ (oxyhemoglobin). Oxyhemoglobin is a *stronger acid* than HHb. Therefore, $HHbO_2$ yields a hydrogen ion to the HCO_3^- ion:

$$HHbO_2 + HCO_3^- \rightarrow HHCO_3 + HbO_2^-$$

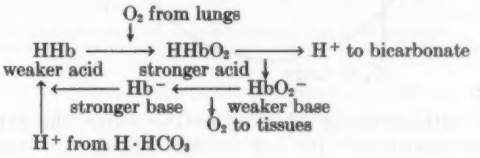
As the HCO_3^- in the cells is used to produce $HHCO_3$, more of these ions diffuse in from the plasma and the Cl^- must then *shift* out of the cells because Na^+ remains in the plasma. The $HHCO_3$ rapidly decomposes into H_2O and CO_2 in the presence of carbonic anhydrase and the CO_2 is thus excreted. Therefore, the blood leaves the lungs with a lower HCO_3^- concentration. There is only a very slight change in the pH of the blood because the hydrogen ions are simply transferred from one base to another.

As the blood passes through the tissues, O_2 diffuses out of the erythrocytes as it is released from the oxyhemoglobin. The Hb^- formed is a *stronger base* than HbO_2^- and it readily accepts H ions from $H \cdot HCO_3$:

$$\underset{\text{weaker base}}{HbO_2^-} \rightarrow O_2 + \underset{\text{stronger base}}{Hb^-}$$

$$Hb^- + H \cdot HCO_3 \rightarrow HHb + HCO_3^-$$

As the bicarbonate ions are formed in the red blood cells, they diffuse out and Cl ions *shift* in because the K^+ remains in the cells. Carbon dioxide diffuses into the red blood cells. In the presence of carbonic anhydrase, this CO_2 rapidly combines with H_2O to form more $H \cdot HCO_3$, which in turn yields more H ions to the Hb^- as fast as it is formed. One can see that the major portion of CO_2 is carried as HCO_3^-, while the hemoglobin of the cells is responsible for the CO_2-carrying capacity of the blood. From this mechanism it is not difficult to understand why the pH of the blood remains so constant as it picks up and yields CO_2. Hemoglobin is continually going through the following cycle:



Oxygen is continually leaving the lungs while CO_2 is leaving the tissues. Therefore one need only to use reason to conclude that $H \cdot HbO_2$ is a stronger acid than HHb. To illustrate this point, let us consider CO_2, which enters the erythrocytes and combines with H_2O to form $H \cdot HCO_3$. Hydrogen ions from this acid do not go to H_2O or there would be a change of pH. Instead, nature must provide a stronger base to accept these H ions. This base must be provided as the O_2 leaves the oxyhemoglobin of the blood:

$$\underset{\substack{\text{weaker}\\\text{base}}}{HbO_2^-} \rightarrow \underset{\substack{\text{stronger}\\\text{base}}}{Hb^-} + O_2$$

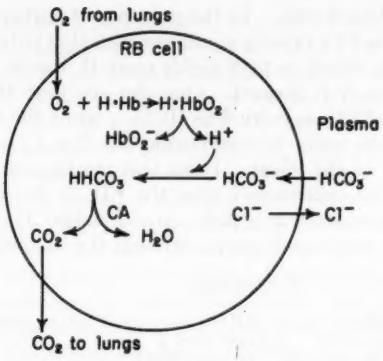
Therefore it is logical to conclude that hemoglobin is the *stronger base* and oxyhemoglobin is the *stronger acid.*

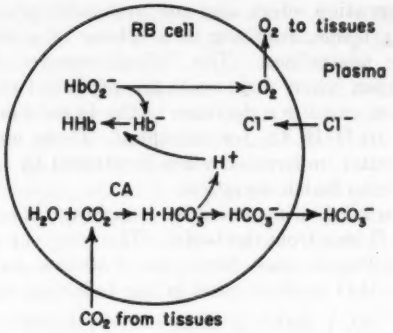
In the charts on the following page, ionic equations are used to illustrate the respiration cycle.

This cycle does not show Na^+ and K^+ because they do not shift across the membrane. The K ions are "companions" to the anions within the cells and the Na ions are "companions" to the anions of the plasma. They themselves do not have a basic action. It should also be remembered that there is an equilibrium existing between ionized and unionized forms of HHb and $HHbO_2$.

SUMMARY

The Brönsted theory shows that there is a direct correlation between acids, bases, and pH. The application of the theory clearly explains the amphoteric behavior of proteins and amino acids and one need no longer think of the hydrated molecules as in the case of the Arrhenius theory. The basic behavior of HCO_3^- is emphasized, while Na^+ and K^+ are shown to be necessary as "companions" to the basic anions. It is not difficult to understand why such cations were called bases before the Brönsted theory was introduced. The theory helps to explain the CO_2-carrying capacity of the blood by showing how $H \cdot HbO_2$ furnishes H ions to the HCO_3^- and how $H \cdot HCO_3$ furnishes H ions for basic Hb^-. When the H ions are transferred from acid to





base without being taken up by the water, the pH remains constant. By aid of the Henderson-Hasselbalch equation, the theory emphasizes the importance of the base-to-acid ratio. In addition, this mathematical expression is easier to understand when the theory is applied. As one would expect, more base tends toward a higher pH and more acid tends toward a lower pH.

In a few words, one can say that the Brönsted theory "puts the action where it is," which helps to avoid confusion, and therefore it should be the approach to the explanation of acid-base balance. Theories have changed and we now have a better understanding of acidic and basic behavior of matter.

The basic action of fruits and vegetables is easily explained by the fact that the organic acids in such foods are utilized by the body, and the organic anions in these foods accept protons from $H{\cdot}HCO_3$ to produce more HCO_3^- base, while the K^+ and Na^+ act as "companions" to the base. Protein foods produce an acid reaction because they yield H_2SO_4 and H_3PO_4, which are not utilized and must be neutralized and excreted.

PROPER PLACE PROBLEMS

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Every chemist has either answered or asked, at one time or another, questions which call for the arrangement of a number of items in correct order. These questions might be termed "proper place problems" since they demand tabulation of things in a correct or proper place.

A typical example might well require the examinee to "arrange in order of decreasing acidity the substances *water*, *ammonia*, *hydrogen fluoride*, and *methane*." Does the student who writes

HF	
NH_3	*X*
H_2O	*X*
CH_4	

know anything about the ionic character of bonds? If it is decided that he does, what should be the part credit assignment?

Questions concerning boiling points frequently take this form since these can be difficult to ask in some of the other ways. "Arrange the following substances, all of which have approximately the same molecular weight, in order of decreasing boiling point: *1-butene*, *n-propyl alcohol*, *methyl formate*, *n-butane*, *acetic acid*, and *acetone*."

1-Butene	*X*
n-Propyl alcohol	
Acetic acid	*X*
Methyl formate	
Acetone	*X*
n-Butane	*X*

Does the above response deserve any credit?

It should be pointed out that such "proper place" questions invite grading by a detailed mathematical system that bears little relation to the more frequently

employed percentile calculations. Consideration of this system by others is hereby welcomed.

The person who selects the uniquely correct answer from among many deserves, naturally, the best score. However, a fact frequently not appreciated is that many answers, even those with several items misplaced, are very difficult to come by through chance and therefore demonstrate knowledge. Table 1 reflects the ease of obtaining any given answer; the values therein have been calculated by the customary combinatorial methods.[1]

It is now suggested that the examinee be given credit for any answer in accordance with the difficulty of obtaining the answer by chance, *i. e.*, be given credit for the extent to which he defies the laws of probability. Such defiance represents, after all, prior knowledge.

If credit is to be proportional to that distance traveled on the road to the uniquely difficult answer, such credit can be calculated from the expression

$$\frac{Z_N - Z_x}{Z_N} 100$$

Table 2 makes this suggestion.

According to the system suggested by Table 2, the student who arranged four acids with two correct does not receive 50 per cent but only 33 per cent, while he who tabulated six substances according to boiling point with two correct merits 50 per cent, not 33 per cent. The more customary percentile assignments have been reversed. Initially surprising, this turn of events need not find its sole support in combinatorial intricacies. Thoughtful consideration of two questions aids clarification: did not each student correctly place two items only? Did not he who faced six items skirt successfully many more pitfalls?

In conclusion, it might be pointed out that several suggestions made by Table 2 are at variance with customary practice in grading "proper place problems." These suggestions merit emphasis.

(1) When a long series of items is involved, no credit should be given for the act of arranging one item in its proper place.

(2) When a long series of items is involved, the act of placing two items correctly merits fifty per cent.

(3) A very substantial portion of credit (80 per cent or over) should be given for the act of arranging any long series of items with more than two placements correct.

TABLE 1

Tabulation of Z_x, the Number of Ways of Arranging N Items with X Incorrectly Placed

Items arranged N	Z_0	Z_1	Z_2	Z_3	Z_4	Z_5	Z_6	Z_7
1	1	0						
2	1	0	1					
3	1	0	3	2				
4	1	0	6	8	9			
5	1	0	10	20	45	44		
6	1	0	15	40	135	264	265	
7	1	0	21	70	315	924	1855	1854

Note that the sum of each horizontal line is N factorial.

TABLE 2

Tabulation of Suggested Partial Credit To Be Given for Any Answer to the Problem of Arranging Items in Correct Order

Items arranged	*Number of mistakes* 0	1	2	3	4	5	6	7
0								
1	100%							
2	100%		0					
3	100%		0	0				
4	100%		33%	11%	0			
5	100%		78%	55%	0	0		
6	100%		98%	85%	49%	0	0	
7	100%		99%	96%	83%	50%	0	0

[1] The calculation of Z_x was made using the expression

$$Z_x = \left(\frac{N}{x}\right) Q_x$$

in which (N/x) represents

$$\frac{N(N-1)\ldots(N-x+1)}{x(x-1)\ldots(1)}$$

in accordance with the notation used by W. Feller in "An Introduction to Probability Theory and Its Applications," John Wiley & Sons, Inc., New York, 1950. Q_x should be read as "the number of ways of arranging x items with none in its proper place" and can be calculated from either of two expressions:

$$Q_x = xQ_{x-1} + (-1)^x$$

or

$$Q_x = x! - \sum_{i=0}^{x-1} \left(\frac{x}{i}\right) Q_i$$

This latter expression can be read as "the number of ways of arranging x objects with all items misplaced is equal to the total number of ways of arranging them less the number of ways of arranging them with less than x misplaced."

THERE are now 67,000 science teachers in the public secondary schools. It is estimated that by 1965 we will need 100,000 to handle the increased enrollments. Where are these new ones to come from, and *why?*

THE EXAMINATION QUESTION

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THE question discussed here is not, "Should examinations be abolished?" but the examination question itself: its nature and content and its relationship to teaching method, especially as applied to the teaching of chemistry. But in considering the nature of the examination question, it is impossible to avoid the question, "Should examinations be abolished?" because it seems to me this question has its origin in widespread misunderstanding of what should be the nature of examination questions and the purpose of examinations.

The examination is a powerful educational tool, but it is neither a sword of Damocles with which the instructor can induce the student to cram information nor is it solely a gage of student achievement. It is a means of directing student thinking and study into profitable channels. This is very likely what Alfred North Whitehead had in mind when he wrote in his essay, "The Aims of Education":[1]

> And I may say in passing that no educational system is possible unless every question directly asked of a pupil at any examination is either framed or modified by the actual teacher of that pupil in that subject. The external assessor may report on the curriculum or on the performance of the pupils, but never should be allowed to ask the pupil a question which has not been strictly supervised by the actual teacher, or at least inspired by a long conference with him.

Although this was published in this country as long ago as 1929 a recent textbook on education states, "Educators are just becoming aware of the potential value of the examination as a means of guiding the student into correct study habits."[2]

I can illustrate the meaning of this from my own experience as a student-teacher. When I first saw, in Appendix I to the sixth edition of Hildebrand's "Principles of Chemistry," the sample examination question,

> Given that the elements A, B, C, D, and E have atomic numbers (nuclear charges) of 6, 9, 13, 19, and 30, respectively . . . Which of the following complex ions are stable? $C(NH_3)_4^{++}$, $D(NH_3)_2^{+}$, $E(NH_3)_6^{+++}$, $E(NH_3)_4^{++}$.[3]

I became aware that my own education in the principles of chemistry was incomplete. I became curious to learn the principles of electronic structure and complex-ion formation by which one could make the correct choice in answering this question.

This type of question stimulates thought and study. Used on an examination, it tests a student's understanding of a useful principle and his ability to use that principle to solve a specific problem; it stimulates him to think in terms of principles rather than to rely on rote memory of facts; and if he has not mastered or understood the principle by the time he meets the question on an examination, it stimulates him to study and learn the principle because it shows him that the principle is something useful.

I assume that chemistry is a science built up of a limited number of useful principles, each with some degree of generality in its application; and I conclude that the learning of chemistry is primarily a mastery of these principles, mastery meaning an ability to use them with facility and, where necessary, with critical evaluation. There is a great deal of factual information within the body of chemical knowledge, of course, but the quality of a person's chemical education is not to be gaged either by the nature or by the number of facts he has in his head, but rather by the way he holds the information and by what he is able to do with it.

Now the development of useful skills, rather than the transmitting of a mass of information, has long and widely been accepted as a valid principle and a worthy aim of education. But the principle itself has been tossed about as a fact and ignored as a guide to action, just as the principles of democracy and Christianity are embraced by millions of persons who continue to act in an autocratic and un-Christian manner. And so questions which require no more of the student than recall of information read in a text or given in a lecture continue to make their appearance on college examinations in chemistry.

An examination is an expression of a philosophy of education. Study a formal examination and you will be able to outline its author's educational objective—is it information or understanding?—regardless of what he says his objective is and of what philosophy he preaches. His behavior in composing the examination speaks louder than his words.

Therefore, teaching will be done with the examination in mind, rather than basing the examination on what has been "covered" and what the teacher thinks he has taught. In outlining the course the teacher will first tabulate the types of problems he expects his students to be able to solve with ease after they have completed the course. These are his objectives. The

[1] WHITEHEAD, A. N., "The Aims of Education and Other Essays," The New American Library of World Literature, Inc., New York, p. 16.

[2] BOSSING, N. L., "Teaching in Secondary Schools," Houghton Mifflin Co., Cambridge, Mass., 1952, p. 247.

[3] HILDEBRAND, J. H., "Principles of Chemistry," 6th ed., The Macmillan Co., New York, 1952, p. 424.

actual teaching, then, will comprise a presentation of principles, the fewer the better, illustrations to make them clear and to show that they pertain to reality, and a working out of sample problems before the class. Learning on the student's part will be by doing and seeing, by working out sample problems which make use of the principles and which show him their utility and their relationship to reality.

Where the ability to solve problems and answer questions by the application of useful principles is the objective of teaching, the student is always in a position to evaluate his own development and to know where he needs more practice. He knows (the teacher should tell him forthrightly) what he is expected to be able to do to make a score of 100 per cent on the final examination. This is not the case when the student is simply "held responsible for" all the material in so many chapters of a textbook. There is always the chance that something will be asked on the final examination which the student did not think was important enough to memorize. No one should be penalized for not knowing at the time of an examination an obscure fact which those who got credit for knowing will have forgotten a month later. A frank and honest statement by the teacher of what is expected of each student should help to relieve the tension often associated with examinations and places the responsibility for mastery squarely upon the student. The results of the examination then will measure not so much the students' memories of uncorrelated facts as it will the teacher's ability to instill understanding of principles and to inflame his students with enough desire to learn and to understand that they will do their homework regularly.

In summary, this article is a plea for more care in the composition of examinations and examination questions, for the use of questions which test mastery of well-defined skills, for making the development of these skills the objectives of teaching, for a forthright statement of these objectives to the students, and for the abolition of the practices of using examinations (quizzes) as inducements to study and of giving examinations solely to establish a distribution of grades—practices which engender the question, "Should examinations be abolished?" and invite the answer, "Yes."

A KINETIC ANALOGY

ROBERT LEMLICH
University of Cincinnati, Cincinnati, Ohio

In teaching chemical kinetics, the conducting of a suitable quantitative demonstrative experiment is often something of a problem. Preliminary preparation of solutions, standardization, and carefully timed titrations are usually required. To circumvent these difficulties an analogous kinetic experiment involving a physical process can be performed which is much simpler and yet which clearly demonstrates the principles involved in a first-order reaction.

The analogy is based on Poiseuille's law for the viscous flow of fluids. According to this relationship the rate of flow for a given liquid at constant temperature through a capillary of given dimensions is proportional to the pressure drop across the capillary. Where this pressure drop is due solely to gravity head in a reservoir of constant horizontal cross section, the rate of fall in height, $-dH/d\tau$ for the liquid level in the reservoir, becomes proportional to the height of the level itself, or,

$$\frac{dH}{d\tau} = -k'H \tag{1}$$

Rearranging and integrating without limits yields

$$\ln H = -k'\tau + K' \tag{2}$$

Equations 1 and 2 are exactly analogous to those for a first-order irreversible chemical reaction where the rate of decrease in the concentration of the reactant $-dc/d\tau$ is proportional to the concentration itself, or,

$$\frac{dc}{d\tau} = -kc \tag{3}$$

A similar integration of equation 3 without limits yields

$$\ln c = -k\tau + K \tag{4}$$

The similarity between the two sets of equations, and therefore the analogy between the two types of kinetic phenomena, is obvious. The gravity-head driving

force in the first set corresponds to the concentration driving force in the second set. Thus a simple demonstration involving a falling liquid level can be employed to illustrate a kinetic "reaction."

The equipment required consists of an ordinary 50-ml. buret, clamped vertically in the usual manner, with a 6-inch length of capillary tubing connected to its tip with rubber tubing. The capillary is clamped in position so that its free end is at the same level as the 50 ml. mark on the buret, as shown in Figure 1. The buret is filled with water at room temperature, partially drained to force out air, and refilled above the 0 ml. mark. The stopcock is then opened wide and the liquid level allowed to fall. The time is noted as the level passes half a dozen or so well-spaced ml. marks. By subtracting these ml. readings from 50 ml. a measure of the height of the liquid level is obtained for various instants. Plotting these heights against the elapsed time on semilogarithmic coordinates yields a straight

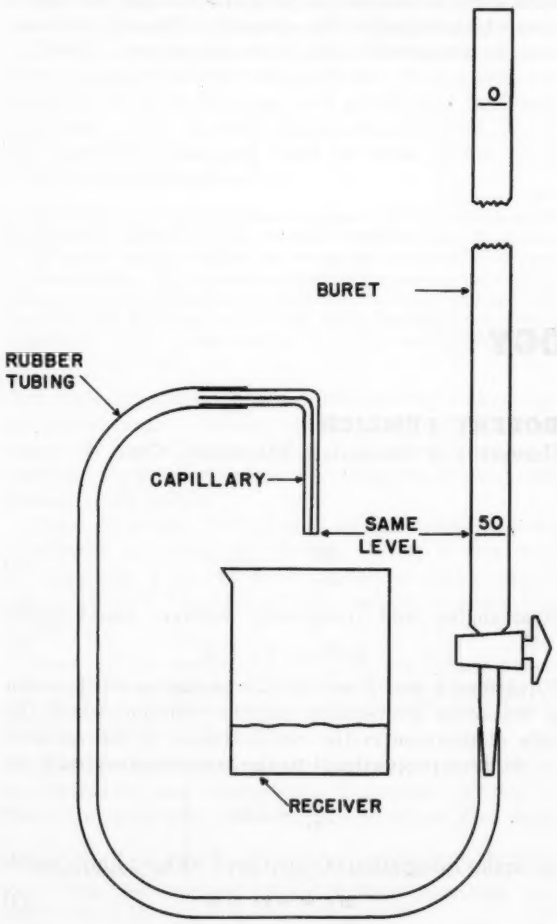

Figure 1. Buret Assembly

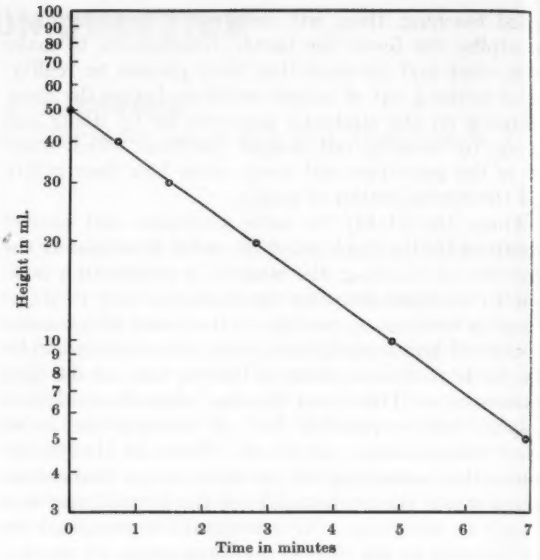

Figure 2. Rate of Change in Liquid Level

line from which k' may be determined, thus demonstrating the validity of equations 1 and 2 and therefore by analogy also equations 3 and 4. Figure 2 shows a plot of such experimental data.

The analogy may be extended even further. For example, the temperature of the water may be increased, thus decreasing its viscosity and in turn increasing k'. For moderate changes in temperature, the logarithm of the viscosity is linear with the reciprocal absolute temperature $1/T$. By combining this fact with Poiseuille's law it can be shown that the logarithm of k' itself is linear with $1/T$. This is analogous to the situation for a chemical reaction where, according to the integrated form of the Arrhenius equation for moderate changes in temperature, the logarithm of the velocity constant k is also linear with $1/T$. In this manner the effect of temperature on reaction rate may be demonstrated.

Another extension of the principle involves the use of two burets in series, the first feeding the second, and the second feeding the receiver. This represents two consecutive chemical reactions. The initial rise, attainment of a maximum, and subsequent fall of the liquid level in the second buret is analogous to the initial increase, attainment of a maximum, and subsequent decrease in the concentration of the intermediate compound. Thus the principles involved in a series reaction may be demonstrated.

In conclusion, it might be pointed out that these experiments not only aid in the teaching of chemical kinetics as such, but serve to introduce the student to some aspects of the fundamental similarities between the kinetics of chemical and physical processes.

THE QUANTITATIVE ANALYSIS NOTEBOOK

C. KINNEY HANCOCK
The Agricultural and Mechanical College of Texas, College Station, Texas

EVEN though fill-in type laboratory notebooks have become increasingly popular in general chemistry and in elementary organic chemistry, apparently most instructors of elementary quantitative analysis prefer to allow students more freedom in writing laboratory notes. In order to check on this apparent trend, the writer, in the summer of 1952, mailed requests for inspection copies of fill-in type laboratory manuals for elementary quantitative analysis to all publishers who had advertisements or listings in the classified catalogue of books in the September, 1951, issue of THIS JOURNAL.

Determination of Na_2CO_3 in Soda Ash
Experimental and Calculated Data

Number of determination	*1*	*2*	*3*	*4*
Tare + soda ash, g. (A)				
Tare, g. (B)				
g. soda ash ($C = A - B$)				
HCl, 2nd buret reading (D)				
HCl, 1st buret reading (E)				
HCl, ml. used ($F = D - E$)				
Indicator blank, ml. HCl (G)				
Corrected ml. HCl ($H = F - G$)				
g. Na_2CO_3 (I = antilog Q)				
% Na_2CO_3 (J = antilog T)				
Deviation, parts per 1000 (K = deviation of J's from L)				

Av. % Na_2CO_3 (L = av. of J's)_____
Av. deviation, parts per 1000 (M = av. of K's)_____

Calculations

Number of determination	*1*	*2*	*3*	*4*
Log corrected ml. HCl ($N = \log H$)				
Log normality of HCl (O)				
Log 0.053002 (P = log meq. wt. Na_2CO_3)	$\bar{2}.72430$	$\bar{2}.72430$	$\bar{2}.72430$	$\bar{2}.72430$
Log g. Na_2CO_3 ($Q = N + O + P$)				
Log 100 (R)	2.00000	2.00000	2.00000	2.00000
$Q + R$				
Log g. sample ($S = \log C$)				
Log % Na_2CO_3 ($T = Q + R - S$)				

Replies were received from 75 per cent of those publishers, and it was found there was only one fill-in type manual available[1] (assuming none available from publishers who did not reply). This manual contains both laboratory procedures and fill-in type data tables but does not contain fill-in type calculation tables.

A mimeographed fill-in type laboratory manual and notebook for elementary quantitative analysis has been used successfully by the writer at The A. and M. College of Texas. A helpful, novel feature of this notebook is the use of fill-in type logarithmic calculation tables which are integrated with fill-in type experimental data tables. Believing that the use of such tables may be of interest to other instructors of quantitative analysis, one example is presented along with pertinent discussion.

It has been observed that such fill-in type calculation tables encourage systematic, accurate calculations, allow the student and instructor to check calculations quickly, and provide good training for the student that would help him in later independent efforts. It has been noted directly that students make fewer errors when using the fill-in calculation tables than they did when allowed to use less systematic methods. A brief inspection of the example given below will indicate the ease of checking calculations both by the student and by the instructor. In advanced quantitative analysis, where calculation methods are less rigorously defined, it has been observed that students who had used the fill-in calculation tables in the earlier course continue to use them or a modification of them and perform calculations more quickly and more accurately than do transfer students who are not acquainted with them.

It should be pointed out that the fundamental basis for the fill-in calculation table is systematic, stepwise calculation as opposed to the use of formulas. As a result, the fill-in calculation tables, as presented, will be of little or no use to the instructor who prefers to use formulas for calculations.

The use of fill-in tables in volumetric analysis is illustrated in the table. Parenthetical notes are given in each line to explain briefly how the tables are used. These explanatory notes may not necessarily be needed by the student; however, if they are not used, the student will need simple, preliminary instructions in the use of the tables. Logarithms of fixed numbers are given in the tables to aid students as a guide in the use of logarithms and in keeping data in alignment.

The writer already realizes that the format of the

[1] CLIPPINGER, D. R., "Manual of Quantitative Analysis," Ginn and Co., Boston, 1947.

elementary quantitative analysis notebook is a controversial issue as a result of differences in philosophy of instruction and of differences in objectives of students. Some instructors prefer leaving the student a large amount of latitude so that he will have experience in developing his own notebook. However, the use of a fill-in type notebook gives the student a great deal of guided drill in his formal course work and might even better prepare the student for keeping his own notebook later on. Such a formalized notebook would have much greater value for large classes in several sections (especially of nonchemistry majors) than it would have for smaller classes of chemistry majors in small liberal-arts colleges, because it simplifies grading and makes for fewer errors on the part of the student. Instructors who are opposed to the use of fill-in type tables throughout the entire course in quantitative analysis might find the use of such tables desirable for the first volumetric and gravimetric determinations to indicate to the students how to organize the recording of their data and their logarithmic calculations.

In spite of much opposition to the use of fill-in type notebooks in quantitative analysis, the writer believes they may be helpful to some instructors in certain situations, especially to the instructor who is badly overloaded.

"WHAT I FIND HARDEST TO BELIEVE"

SAMUEL WEINER
University of Wisconsin, Wausau, Wisconsin

In an effort to mitigate the oft-mentioned evils of excessive use of objective-type examinations, the monthly and final examinations used in the chemistry classes at the Wausau Extension Center of the University of Wisconsin have included a single essay question. Recently, in the first monthly exam of the year, the essay question was chosen to produce information, not test it: "What I have found most difficult to believe in this course." A study of the responses has led to some observations.

The short and skimpy essays were mainly by students doing poorly in the objective part of the exam and in the other work of the course. Partially, this resulted because the essay question was the last one; a student who had been slow in working the calculations, balancing, or multiple-choice questions would have little time left for organizing and writing an essay. However, it is the belief here that unsatisfactory performance in chemistry is often accompanied by inadequate command of English. The causes seem to be varied: a rural population whose young men are mechanically facile but inexperienced in either clear expression or logical reasoning; poor training in rhetoric in the regional high schools; or the intelligence factors that make for literary skill's being identical with or overlapping those that make for scientific reasoning.

A few students alleged they had found nothing hard to believe. These credulous ones were equally distributed among the upper and lower halves of the class. A few confused "believe" with "understand" and therefore merely made lists of the topics that gave them trouble.

About half of the students expressed doubt of some phase of radioactivity or modern intra-atomic theory. The chief objections the students raised were: the small size of the atoms, the indirect nature of the evidence for atoms or their nuclear components, and the large proportion of empty space in matter according to the atomic theories.

Among the statements were: "I have no possible conception of how tiny particles, invisible to the human eye, can be, when given off, named and given a charge, and furthermore I don't see how scientists have come on to the discovery of the half-life of an element." "Although I like it [radioactivity] very much it remains a sort of mystery to me." "The thing I find hardest to believe, thus far, is that new products are formed as a result of radioactivity." "Practically all one's school years are filled with problems that must be solved in successive steps with tangible proofs for every step. In chemistry one comes to the theory (that most people accept without doubt) that everything is made up of tiny particles, atoms, which cannot be seen. Furthermore, these particles are made up of even smaller units, the electrons, protons, etc. If you cannot see these particles, how can you say they are there?" "What I find hardest to believe is that one is able to work with such a small particle as an atom with any degree of accuracy. It seems incredible that one can tell how many electrons, neutrons, protons are contained in it, and still more in-

credible that one can predict what will happen to them when they unite with another element's atom to form a molecule." "I can't quite believe that an element will throw off rays and lose particles of matter and then suddenly switch into something else as in the case of radium switching into radon."

One of the more intelligent and articulate students wrote: "One thing that I still cannot accept thoroughly is simply the way the chemist works as far as formulating theories and laws goes. Although there is no proof, and it is simply one man's wild guess being accepted by other cohorts in chemistry, these theories are still used and worked with, and even laws are based on them.

"As an example, let us take the atomic theory, it being one of the most wild and yet most accepted and believed. An atom consists of a nucleus and planetary electrons. [At this point the student had a Lewis electron diagram of a three-shell atom.] This atom consists therefore of more vacuum, or empty space, than anything else. According to that, and accepting that everything consists of atoms, the illogical conclusion is that every substance is made up mainly of vacuum, or nothing. And our life is maintained by breathing more vacuum than anything else. There is still much I have to learn about atoms and the like, but what I have learned up to date doesn't seem good enough to be so widely accepted as it is."

The better students were the more frank in expressing a skepticism that appears naïve to experienced teachers. Much of this skepticism as to intra-atomic structure or the atomic theory may be caused by the textbook's treating of intra-atomic and nuclear structure before the determinations of atomic and molecular weight. The latter topic was not reached in this course until after the exam was given, so the students had had to use such concepts as atomic and isotopic weights in calculations without knowing how they are obtained by chemists. This in itself would give to the topic a taste of unreality. The absence of experiment in the college laboratory to show radioactive expulsions or nuclear compositions was remarked on by some of the students. The objection to the wide open spaces in hard matter can be understood; Aristotle and a millenium of churchmen disregarded the Democritean theory because they too could not accept the idea of vacuum. The small size of the atoms and the impossibility of ever seeing them is another permanent defect; a fifth of the students mentioned this.

The periodic system was mentioned by a seventh of the class, but their comments were mainly on its remarkable utility and plenitude of information. One girl wrote: "It seems unbelievable that anyone could conceive the idea of this chart, which although it is not perfect in all respects does classify the elements in order of atomic weight and atomic number and also with like properties in the same groups. It seems unbelievable that all the parts of the chart can be fitted together so perfectly and in accordance with all the laws of mass, valence, etc. Another amazing characteristic of the chart is its ability to predict new elements."

The present writer had expected the kinetic theory of gases to present some unbelievable aspects but only a tenth of the class mentioned it or any of its postulates. This is probably owing to the textbook's giving a clear though qualitative derivation of the gas laws from the kinetic theory after the former had been presented empirically.

It is the writer's belief that the essay question, despite its time consumption, is necessary to develop the student's literary ability by giving him an opportunity to practice under tension the teachings of his intermediate and high-school English classes. It is the custom here to mark errors in grammar and spelling, but not consider them in the grading of the paper. An essay question of the type here used distinguishes between the memorizing of facts and the ability to synthesize judgments. More important, it serves like an anonymous evaluation questionnaire to tell the instructor something of what his students feel.

The inductive order of presentation is better than the deductive for attaining plausibility. The earlier a theory is placed before the students, the greater the difficulty they have with it. In spite of the amount of publicity of nuclear structure, as a concept it is foreign to the physical and mental experiences of the students. They will understand it better and feel more at ease with its postulates if they study it after familiarity with its experimental base, in a later year. The average American college student is empirical-minded. He cannot easily accept a strange hypothesis and deduce from it dogmatically inevitable conclusions.

In this course emphasis has been laid on the scientific mode of reasoning and on a critical attitude toward theories. The students were told to center their attention on the logic of the deduction and to consider a postulate, however unfamiliar or plausible, as a provisional starting point for the deduction. The "scientific method of reasoning" is given lip service in most courses, it being mentioned only in the text and in an early lecture. Here, greater emphasis has been put on it, but students have shown themselves more absorbed by the startling features of the initial postulates than by either the weight of experimental evidence or the rigor of a deduction.

In lectures subsequent to this examination, efforts were made to clear the gaps in the students' information as revealed by the essays.

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Proceedings of the

PACIFIC SOUTHWEST ASSOCIATION OF CHEMISTRY TEACHERS

MEETING OF THE NORTHERN SECTION

THE Pacific Southwest Association of Chemistry Teachers, Northern Section, met late in April for a two-day session in San Francisco. In addition to carrying on the business of the society, members of the Association were privileged to hear interesting lectures by B. M. Tolbert on the use of radioactive tracers and George Gamow on a new theory of the function of the chromosomes in guiding cell replication. On the afternoon of the second day the members met jointly with the science fair sponsored by the National Association of Manufacturers.

Dr. Tolbert, a research chemist at the University of California radiation laboratory in Berkeley, referred to radioactive tracers as tools with which to work on problems in biochemistry. Confining his attention to C^{14}, he showed first how this isotope could be introduced into a molecule of a drug such as codeine, and then how the disposition of the radioactive element could be traced in the human body. According to Tolbert's figures, whereas 90 per cent of the radiocarbon from his specially prepared glycine appears in the breath, only 10 per cent of the radioactive carbon in the drug Demerol is so excreted. From other drugs the radioactive element may appear largely in the urine; with still others most of the C^{14} goes into the feces.

Describing an interesting development of these experiments, Tolbert showed a slide of an ingenious apparatus used to make a continuous record of the C^{14} content in the breath of an experimental animal. The animal was enclosed in a glass bulb through which fresh air was pumped continuously. After leaving the animal the air passed through an ionization chamber. The varying potential of the chamber was automatically recorded and this potential was calibrated to give the concentration of C^{14}.

A number of other experiments were described, including the use of chromatographic adsorption to isolate minute quantities of the radioactive products of photosynthesis. Algae were supplied with carbon dioxide containing C^{14}, light was radiated on the algae for, say, 10 seconds, and the products formed in the algae were separated by chromatography. The variously placed smudges were checked for C^{14} content and analyzed.

Dr. Gamow's lecture was enthusiastically received. His touches of humor and the modest way in which he put forward his proposals were especially appreciated by those fortunate enough to hear him speak. To explain his interest as a theoretical physicist in the problems of cell replication he pointed out that biology, especially the biology of heredity, is rapidly becoming an exact science.

To provide a background for his theory he illustrated mitosis and showed how the long thread-like molecules of desoxyribonucleic acid consist of long lines of pyrimidines and purines, linked to sugar phosphate chains. These filaments are given a helical twist that repeats every ten steps.

The key compounds in the DNA molecule are adenine, thymine, guanine, and cytosine. If these four compounds are numbered one to four, a long and special sequence of four digits, including π and $\sqrt{2}$ may be used to stand, in coded form, for the pattern of a particular living organism. Gamow called this the number of the beast. It is the blueprint in the chromosomes that somehow guides the enzymes toward the peculiar pattern of chemical synthesis that results in an individual similar to others of the species, yet, in many respects, uniquely different.

Next, Gamow linked the proposed pattern for the DNA molecule with the number of amino acids which form in proteins. Arranging the numbers one to four spirally on a mailing tube, he saw immediately that he had a series of diamonds, with one of the four digits marking each base. Numerical consideration indicated 20 different kinds of diamonds. Of the thousands of possible amino acids, only 20 should fit into the slots provided. His hypothesis thus suggests a mechanism whereby the pattern of bases in the chromosomes can be used to stamp out a pattern of amino acids in those proteins that go to build a complete organism.

Verification of the theory has been partially successful. The pattern of amino acids in both insulin A and insulin B has been worked out by Sanger. When a possible intersymbol combination (of which there are 10^{17}) is compared with the insulin patterns, that for A fits, but that for B does not.

In conclusion, Gamow showed some colored slides of beautiful and intricate models by which he had attempted, with only partial success, to portray complete DNA molecules.

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Report of the

NEW ENGLAND ASSOCIATION OF CHEMISTRY TEACHERS

OFFICIAL BUSINESS

275th MEETING

The 275th meeting of the Association was held on Saturday, April 17, at Avon Old Farms, Avon, Connecticut, a boys' preparatory school. The buildings, though less than thirty years old, are replicas of sixteenth-century English buildings with hand-hewn beams. The stone was cut and the glass was made on the premises. The whole layout is unique and very interesting. In spite of heavy rain, 43 attended.

Two interesting papers were given in the morning. Dr. Ralph Nazzaro of Westfield River Paper Company spoke on "Chemistry in the paper industry." He gave us an insight into some of the phases of paper making that we seldom think about. The uses of paper have increased tremendously in recent years, especially in the container field. Then Dr. Francis J. Norton of General Electric Company gave a talk on the "Applications of the mass spectrometer." He presented data to show the use of the spectrometer in research. He illustrated his talk by means of a mechanical model to show the principle of the mass spectrometer.

After a delicious roast beef dinner, Provost Donald W. Pierpont presented an interesting and humorous account of the history and policy of the school.

During the afternoon session, Professor Seward Beacom of State Teachers College, New Britain, Connecticut, gave a thought-provoking paper on the "Teaching of the electromotive series." Before leaving many took advantage of a tour of the school conducted by Mr. W. James Kilgour, to whom we are indebted for arrangements for the meeting.

At a short business meeting, the secretary welcomed the following new members into the Association:

Philip Bronspiegel, Chemistry Teacher, New Bedford High School, New Bedford, Massachusetts.

Constance Wight Carney, Assistant in Chemistry, Connecticut College, New London, Connecticut.

Philippa G. Gilchrist, Associate Professor, Wellesley College, Wellesley, Massachusetts.

Helen G. Husted, Assistant Professor, Regis College, Weston, Massachusetts.

John W. Kimball, Instructor, Noble and Greenough School, Dedham, Massachusetts.

Colin Livesey, Science Instructor, Boston University Junior College, Boston, Massachusetts.

George J. Overlander, Instructor, University of Massachusetts, Amherst, Massachusetts.

John E. Teasdale, Master in Chemistry, Seymour High School, Victoria, Australia.

It was voted to send thanks to Avon Old Farms for the hospitality of the day.

NECROLOGY

WILLIAM O. BROOKS. On April 9, 1954, at his home in Wilbraham, Massachusetts, Colonel "Will" Brooks, our former Secretary and Division Chairman, and a member of the NEACT since March 5, 1921, died.

He was born in Somerville, October 10, 1894, and graduated from Harvard College in 1917. He later received his master's degree from its Graduate School. He was a General Electric fellow.

Before coming to Springfield in 1924, he taught chemistry in Colchester, Rockville, and Willimantic in Connecticut, and in Springfield, first in the High School of Commerce, and since 1936, in the Technical High School.

For five years previous to World War II he held the office of secretary of the NEACT, 1936–41, and will be remembered for his outstanding work in converting the old *Report* into the quarterly magazine format. He also served as chairman of the Western Division of the NEACT, 1948–50, as secretary of the Fifteenth Summer Conference in 1953, and as a member of the Necrology Committee, 1952–53.

His military career began in 1930 when he enlisted as a private in the Army Reserve Corps; he became a lieutenant in 1931 and a captain in 1938. Called to active service in 1941, he served in the Chemical Corps in several capacities, rising through various grades, and becoming a colonel in 1946.

He will be remembered as a competent author of science work books and as a co-author of science textbooks with Dull.

S. WALTER HOYT
Chairman, Necrology Committee

276th MEETING

Saturday, May 16th, was the occasion of the 276th meeting, held at Emmanuel College, Boston. Approximately 70 members attended; this was also the occasion of the Annual Meeting.

The first speaker of the morning session was Edward Shapiro, of Tracerlab, Inc., Boston, whose topic was "Laboratory Experiments with Radioisotopes." Dr. Shapiro demonstrated experiments selected from the recently published U. S. A. E. C. manual, "Laboratory Experiments with Radioisotopes for High School Science Demonstrations," by Samuel Schenberg, published by the U. S. Government Printing Office in 1954 (25 cents). He also gave some lecture demonstrations of his own design.

Ralph E. Keirstead, the second speaker of the morning, of Bulkeley High School, Hartford, Connecticut, and member of the NEACT, gave an informative and interesting account of his "sabbatical," or pedagogical

reprieve, 1952–1953, sponsored by the Ford Foundation which was spent in touring the United States to study the sources of the "Raw materials for the American economy." His paper drew important conclusions about information on mineral conservation that should be introduced into the chemistry course.

The afternoon speaker was Rev. Bernard A. Fiekers, S.J., Chairman of the Department of Chemistry, College of the Holy Cross, Worcester, Massachusetts. His talk centered on various "Techniques for teaching some topics in general chemistry," and included graphical methods and other teaching techniques as applied to determining the sensibility of the analytical balance, law of definite composition, and special problems in teaching dynamic equilibria.

The President, Dorothy W. Gifford, opened a brief business meeting.

The secretary welcomed four new members into the Association:

John A. Meegan, Head of Science Department, Framingham High School, Framingham, Massachusetts.
Forrest H. Page, Head of Science Department, North Attleboro High School, North Attleboro, Massachusetts.
Sister Magdalen Julie, Instructor, Emmanuel College, Boston, Massachusetts.
Sister Mary John Hoye, Chairman of Chemistry Department, Emmanuel College, Boston, Massachusetts.

Robert D. Eddy, Chairman of the 16th Summer Conference, gave a detailed report of the program and arrangements at Amherst.

Carroll B. Gustafson, Treasurer, reported informally on the condition of the treasury. The final report for the year will be presented at the time of the Summer Conference.

Balance, August 1953	$1216.34
Summer Conference Surplus	215.75
Dues, 570 members	2247.50
Income	$3679.59
Disbursements	1937.23
Balance on Hand, May 15, 1954	$1742.36

This balance indicates that the Association at the end of the fiscal year will show a net gain in income.

A vote of thanks to Emmanuel College for its hospitality was taken.

The meeting was adjourned and the Annual Meeting immediately convened.

ANNUAL MEETING

Emmanuel College, Boston, Massachusetts, May 15, 1954. Dorothy W. Gifford presided at the annual meeting. The following reports were accepted:

Secretary's Report. The Fifteenth Summer Conference was held at Bowdoin College, Brunswick, Maine, with John E. Cavelti (by remote control) and Guy F. Burrill as Co-Chairmen.

During the year five meetings were held with the attendance shown:

272nd:	Spaulding High School, Rochester, New Hampshire, October 10, 1953.	29
273rd:	Brandeis University, Waltham, Massachusetts, December 4, 1953.	98
274th:	East Providence High School, East Providence, Rhode Island, February 13, 1954.	77
275th:	Avon Old Farms, Avon, Connecticut, April 17, 1954.	43
276th:	Emmanuel College, Boston, Massachusetts, May 15, 1954.	71

The secretary announced that Laurence S. Foster had been reappointed by the Executive Committee as Editor of the *Report*.

The secretary also reported for the Membership Committee: Number of members suspended for nonpayment of dues, January 1, 1954, 48. Of these 22 were later reinstated, 7 resigned, and 19 dropped from the rolls.

Forty-nine new members were taken in during the year, 10 at the Summer Conference. Of these 27 are high-school teachers, 19 from colleges and three from industry.

The total membership on May 15, 1954, was 571.

LEALLYN B. CLAPP, *Secretary*

Report of the Treasurer of Endowment Fund, May 15, 1954.

Balance, May 9, 1953	$2381.40
Income credited from May 5, 1953 through May 7, 1954:	
Watertown Federal Savings and Loan Association	20.00
Newton Savings Bank	38.79
Two per cent of dues, 1952–53	44.80
New balance, May 7, 1954	$2484.99
Investments, May 7, 1954:	
Five matured shares, Watertown Federal Savings and Loan Association, at cost	994.91
Balance in Newton Savings Bank, May 7, 1954	1490.08
Balance, May 7, 1954	$2484.99

AVERY A. ASHDOWN, *Treasurer*
Trustees Permanent Trust Fund

Report of the Curator for 1953–54. During 1952–53, the Curator was on leave of absence. Consequently, the major task of this year has been to bring the membership file up to date. That has been done. It may be of some interest to know that, since the founding of the New England Association of Chemistry Teachers in 1898, 1941 members have been admitted up to April 17, 1954.

Each year a number of requests for information come to the curator about items that have appeared in the *Reports* and about the activities of the Association. The bound volumes of the *Reports* and the permanent membership file make it easy to comply with such requests.

At the request of Mr. Louis Panush, editor of the *Journal of the Metropolitan Detroit Science Teachers Association*, the Curator prepared an article about the history, organization, and present activities of the Association. The article appeared recently.

RALPH E. KEIRSTEAD, *Curator*

Laurence S. Foster, Editor of the *Report* and of the *News Letter*, gave an informal report. He suggested that the office of Assistant Editor of the *Report* should be discontinued. He intends to appoint several reporters for the *News Letter* to get better coverage of activities of individual members. Eva M. Ruggli was reappointed Assistant Editor of the *News Letter*.

Anne R. Kelley gave a report on the completion of the "Syllabus for Nursing Students" by the Committee (Margaret Parks, Raymond Neal, and Anne Kelley). It is to be duplicated in time to be available at the Summer Conference. It was suggested that a note be made in the *News Letter* that anyone wanting one mailed could obtain a copy by writing to Dr. Margaret Parks, University of Rhode Island, Kingston, Rhode Island.

Report of the Honorary Membership Committee. The Honorary Membership Committee nominated the following members for honorary membership, who were duly elected unanimously:

GROVER C. GREENWOOD. Grover C. Greenwood has been a member of the New England Association of Chemistry Teachers for 31 years. He has served this organization as a member of committees and as a participant in programs on numerous occasions. He is one of that small company which has attended every Summer Conference. His long and devoted service as a teacher of chemistry will end with his retirement from Harding High School, Bridgeport, Connecticut, in June.

MARY L. SHERRILL. Mary L. Sherrill is recognized as a chemist of distinction, as a departmental chairman of high capabilities and as a teacher of unusual charm and effectiveness. She has addressed this Association on several occasions. Her interest in the things for which the New England Association of Chemistry Teachers stands is attested by her 30 years of membership.

RAYMOND S. TOBEY. Raymond S. Tobey has been a member of the New England Association of Chemistry Teachers for 40 years. During that time he has accepted many calls for his services by the Association as duties to be faithfully discharged. By his long career as a teacher he has set rigorous standards for himself and his pupils, always adhering to the principle that the thing which should be done is that which is *right* to do. He exemplifies all that is fine in that legendary figure—the New England Schoolmaster. His skill as a teacher is strikingly demonstrated by the fact that one of his students has just received the $1000 Bryn Mawr Award for the best essay on radioactivity.

LAURENCE S. FOSTER. Laurence S. Foster is a person whose restless energy has made him willing to accept, almost from the day of his election to membership 24 years ago, responsibilities in the operation of the New England Association of Chemistry Teachers which are continuing today. Few persons have done more to make this Association strong. Although he chose to leave the academic lecture hall and laboratory for other pursuits, he is still the teacher, for his many addresses before the NEACT have done much to stimulate the thinking of other teachers.

Guy F. Burrill was elected a member of the Nominating Committee to serve for three years in place of Amasa F. Williston, whose term of office expires. Other members of the committee are Helen W. Crawley and Carl P. Swinnerton.

Election of Officers. The Nominating Committee proposed the following to serve as officers for the year 1954–55, who were duly elected unanimously:

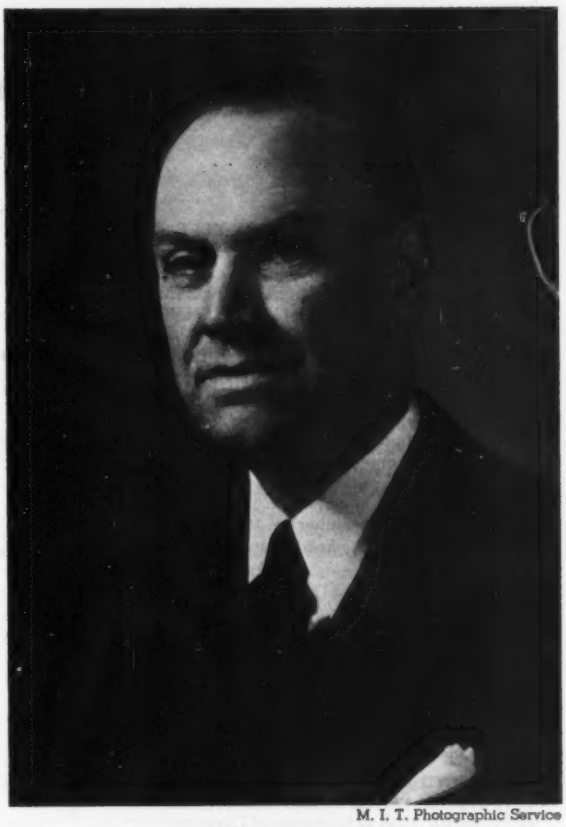
President.....John A. Timm, Simmons College.
Vice-President...Marco H. Scheer, Nashua High School.
Secretary.....Leallyn B. Clapp, Brown University.
Treasurer.....Carroll B. Gustafson, Massachusetts College of Pharmacy.
Chairman of Northern Division...Lorne F. Lea, St. Paul's School.
Chairman of Central Division....Dorothy Abel, Brookline High School.
Chairman of Western Division....E. Harold Coburn, Bulkeley High School, Hartford.
Chairman of Southern Division...Evelyn L. Murdock, Stonington High School.
Trustee of Endowment Fund.....Mary B. Ford, Milford, Massachusetts.

A vote of thanks to the retiring officers was passed unanimously.

Dorothy Gifford turned over the gavel to the new President, John A. Timm, with appropriate remarks.

LEALLYN B. CLAPP, *Secretary*

JOHN ARREND TIMM was born in New Haven, Connecticut, on October 31, 1898. In 1919 he received the Ph.B. degree from the Sheffield School of Yale University. After serving as a second lieutenant in the Field Artillery in World War I, he received his Ph.D. degree from Yale in 1922 and served on its chemistry faculty until 1941. While at Yale he developed one of the first courses in this country in chemistry for the liberal-arts student, and in 1938 published "An Introduction to Chemistry," which has now gone through three editions, as a textbook for this type of course. In 1941 he became Director of the School of Science and Chairman of the Chemistry Department at Simmons College, Boston, Massachusetts. His "General Chemistry," a text-



M. I. T. Photographic Service

John A. Timm

book for science majors, appeared in 1944 and was revised in 1950. During his first years at Yale he conducted research work on the structure of cellulose and of heterocyclic compounds and later turned to physical chemistry of electrolytic solutions. Now he is too busy with administrative and teaching problems to have much time for research. Both he and Mrs. Timm are interested in eighteenth-century furniture and their hobbies include the restoration of antique furniture and the high-fidelity reproduction of classical music. The Timms have a porchful of restored Boston rockers for guests to relax in while listening to music!

John Timm served as Chairman of the Northeastern Section of the American Chemical Society from 1951 to 1952. He has also been a Councilor of the Division of

Chemical Education and a member of the Board of Publication of the JOURNAL OF CHEMICAL EDUCATION. Dr. Timm has been an active member of this Association for many years and has served on numerous committees and spoken frequently at its summer conferences and divisional meetings. He is most noted for having originated the idea of the summer conference in 1939.

CORRECTION OF OMISSION

Through a regrettable oversight, no mention was made in the December Report of the splendid illustrated address given at the 15th Summer Conference by Mr. and Mrs. Harold E. Coburn, Bulkeley High School, Hartford, Connecticut, on their year in India.

DIVISION OF CHEMICAL EDUCATION

OF THE AMERICAN CHEMICAL SOCIETY

Officers and Committee Members

*A. B. Garrett, Chairman, September, 1953 to September, 1954
*C. A. VanderWerf, Chairman-elect, September, 1953 to September, 1954
*Paul Fall, Past Chairman, September, 1953 to September, 1954
*Grant W. Smith, Secretary, September, 1953 to September, 1956
*Fred B. Dutton, Treasurer, to September, 1954
*W. H. Steinbach, Member-at-large, Executive Committee, September, 1953 to September, 1956

Councilors

*John Cavelti, to December 31, 1954
*Grant W. Smith (*ex officio*), January 1, 1954 to December 31, 1956

Alternate Councilors

W. E. Morrell, to December 31, 1954
J. F. Corwin, to December 31, 1956

Editor of JOURNAL OF CHEMICAL EDUCATION

*Norris W. Rakestraw

Board of Publication

A. B. Garrett, 1954 as Chairman of Division
F. B. Dutton, 1954 as Treasurer of Division
G. W. Smith, 1956 as Secretary of Division
W. F. Ehret, 1954
M. G. Mellon, 1955
P. W. West, 1956

Committees

Examinations and Tests

T. A. Ashford, Chairman (subject to reappointment by Executive Committee)

Terms expire September, 1954:
O. M. Smith
F. D. Martin
S. S. Cooper
R. L. Van Peursem

Terms expire September, 1955:
C. E. Ronneberg
E. L. Haenisch
O. C. Dermer

Terms expire September, 1956:
G. H. Pritham
L. R. Brantley
D. P. Wright

Subcommittee Chairmen

C. E. Ronneberg, General
R. L. Van Peursem, Analytical
B. A. Nelson, Organic
E. L. Haenisch, Physical
G. H. Pritham, Biochemistry
L. R. Brantley, West Coast Area

Teaching of College Chemistry

	Expiration date
O. M. Smith, Chairman (subject to reappointment by the Executive Committee)	
D. G. Nicholson, Assistant Chairman	1954
J. F. Corwin	1954
L. R. Brantley	1954
J. F. Baxter	1955
G. W. Smith	1955
E. L. Haenisch	1955
B. M. Norton	1956
J. A. Campbell	1956
L. B. Clapp	1956

Code for Employment of Graduate Assistants (appointed 1949-50)

R. C. Anderson, Chairman, University of Texas
J. F. Corwin, Antioch College
A. W. Laubengayer, Cornell University
R. K. Summerbell, Northwestern University
J. E. Willard, University of Wisconsin

Committee to Study Possible Geographical Divisions Within the Division

M. F. Stubbs, Chairman (appointed March, 1953)
J. Fuchs (appointed March, 1953)
B. M. Norton (appointed March, 1953)

Committee to Edit Industrial Films

J. A. Campbell, Chairman (appointed September, 1953)

Representative to AAAS Cooperative Committee on Science Teaching

L. L. Quill, 1954

* Members of the Executive Committee.

Recent Books

CATIONIC POLYMERISATION AND RELATED COMPLEXES

Edited by *P. H. Plesch.* Academic Press, Inc., New York, 1953. xii + 166 pp. 12 figs. Tables. 14.5 × 22.5 cm. $4.

THE title of this book is slightly misleading, for it deals not with cations in any definite respect, but rather with the catalytic effects of various electron-acceptor molecules, such as boron trifluoride, aluminum halides, or tin(IV) compounds, upon the mechanisms of polymerization of organic units. The material is presented in the manner of a symposium of the Faraday Society: a series of research or review papers on various aspects of the subject, each with a bibliography and discussion. The whole effect is to aid the development of ideas for further research, for most of the papers not only present solid facts but also emphasize aspects which are not yet clearly understood. The discussions also help to demonstrate what is yet to be done to improve understanding.

The first section consists of eight papers (plus introduction and summary) devoted primarily to complex-formation between inorganic electron-acceptors and organic substances. Of most interest in relation to the process of polymerization are the arylonium complexes such as $C_6H_7Al_2Br_7$ (Eley), the latest ideas of bonding in the alkene-metal complexes (Chatt), and a survey of the problem of energetics of coordinate bonding (Skinner). The second section is concerned almost entirely with the polymerization processes themselves: styrene and its derivatives, under the influence of $SnCl_4$, $TiCl_4$, Al_2Cl_6, $SbCl_5$, BF_3, and $HClO_4$, with or without hydrogen halides; then alkenes, including carbonium ion reactions. Altogether there are 42 contributors, from five different countries, and it would appear that the original meeting (at the University College of North Staffordshire, March, 1952) must have been a very interesting and high-level occasion. The general tone is nondogmatic and, considering the highly specialized nature of the subject, the breadth of fundamental interests covered is remarkable.

ANTON B. BURG

UNIVERSITY OF SOUTHERN CALIFORNIA
LOS ANGELES, CALIFORNIA

INDUCTION AND DIELECTRIC HEATING

J. Wesley Cable, Consulting Engineer. Reinhold Publishing Corp., New York, 1954. vii + 576 pp. 16 × 23.5 cm. $12.50.

ALTHOUGH induction heating has been used for more than fifty years in the metallurgical industry, dielectric heating is a relative newcomer which is finding uses in a variety of industries. The author says, "I have had one idea in mind, that of telling the engineer, the designer, the heat-treater, the maintenance man, about the practical accomplishments and application of these two new tools for industry, with only a smattering of the theory behind their use. Such will be the tenor of this book."

As would be expected, the first half of the book, on induction heating, deals with metallurgical applications. The second half, on dielectric heating, discusses its applications in the plastics industry, woodworking field, baking foundry cores, food-processing field, sterilization and allied processes, and moisture removal. The chapter on the future of dielectric heating points out interesting possibilities.

If one wants to know the "how" and not much about the "why" of induction and dielectric heating, this book will be of use to him. The potentialities of dielectric heating in the chemical laboratory and chemical industry are great, and the present applications of this form of heating can be read with interest by chemists and chemical engineers.

KENNETH A. KOBE

UNIVERSITY OF TEXAS
AUSTIN, TEXAS

ELSEVIER'S ENCYCLOPAEDIA OF ORGANIC CHEMISTRY. SERIES III: CARBOISOCYCLIC CONDENSED COMPOUNDS. VOLUME 12B: NAPHTHOIC ACIDS AND THEIR HALOGEN, NITROGEN AND HYDROXYL DERIVATIVES

Edited by *F. Radt.* Elsevier Publishing Co., Houston, Texas, 1953. xliii + 595 pp. (text) + 45 pp. (index). 17.5 × 26 cm. Subscription price, $42. Serial price, $49. Single copy, $56.

THIS part of "Elsevier's Encyclopaedia" differs only from the one recently reviewed here (THIS JOURNAL, **31**, 104 (1954)) by coverage of naphthalenes with one carboxyl group attached directly to the ring rather than to a side chain. These naphthoic acids, and also their hydro derivatives and homologues, are listed in respect of halogen and nonfunctioning nitrogen derivatives, as well as of hydroxy and amino compounds. Included, usually after these functioning derivatives, are the lactones and lactams related by the principle of anhydrosynthesis. The proximity of these heterocyclic entries, and others like the cyclic methylene ethers, conforms with the editorial policy of collecting all data pertinent to a key compound as close to it as possible. The resulting convenience during an exploratory literature search is apparent.

The value of this "Encyclopaedia" has once been expressed by the reviewer and needs no repetition. It is evident that the wide adoption of "Elsevier" will not depend upon the question of its desirability but rather upon its cost. The publishers have realized this limitation by offering a "deferred payment plan." Thus those who, sensibly, have waited until the "Encyclopaedia" proved its worth may now acquire it by an arrangement that is convenient to their annual budgetary allotments.

GEORGE F WRIGHT

UNIVERSITY OF TORONTO
TORONTO, CANADA

DETERGENCY EVALUATION AND TESTING

Jay C. Harris, Monsanto Chemical Co., Dayton, Ohio. Interscience Publishers, Inc., New York, 1954. x + 210 pp. 12.5 × 18.5 cm. 26 figs. 15 tables. $3.75.

THE major phases of detergent evaluation, both qualitative and quantitative, are described, with illustrations of several types of equipment. Screening tests include wetting, acid and alkali stability, surface and interfacial tension, lime-soap dispersion, lather values, and others. Results for these are given for ten Monsanto detergent products.

Preparation of standard soiled fabrics includes cotton, wool,

silk, and seven synthetic fabrics. Methods described for evaluating detergency include those with the Launder-Ometer, Terg-O-Tometer, Deter-Meter, home and power laundering, wool scouring, and dry cleaning. Evaluation of detergents for special purposes covers shampoos, cleaning of metals, painted surfaces, linoleum, and dishwashing. Radioisotope tracer techniques are described, also evaluation of fluorescent brightening agents and methods for the study of corrosion of aluminum and vitreous enamel.

Compilation of all these methods into manual form is a great convenience to the detergent chemist.

CORNELIA T. SNELL

FOSTER D. SNELL, INC.
NEW YORK, NEW YORK

● THE ACTINIDE ELEMENTS. VOLUME 14A, DIVISION IV

Edited by *Glenn T. Seaborg*, University of California, and *Joseph J. Katz*, Argonne National Laboratory. McGraw-Hill Book Co., Inc., New York, 1954. xxx + 870 pp. 17 × 23.5 cm. $11.75.

THIS volume has a consistency of treatment of the actinide elements that was missing in the earlier (1950) Parts I and II of Volume 14B, "The Transuranium Elements," which are comprised of a collection of individual research papers. The present volume includes two indexes, one for Volume 14B as well as for 14A. The total of 2648 pages in these three large books on the actinides, all of which were relatively unknown or nonexistent 15 years ago, give better coverage than has been afforded many so-called familiar elements.

While the greatest use of these books will be made by research workers, two sections of Volume 14A will attract the attention of the general reader, namely, the "Introduction" (pages 1 to 13) and Chapter 17 (pages 733 to 779), "Correlation of properties as actinide transition series," both written by Dr. Seaborg. The latter chapter is reminiscent of his address before the Division of Chemical Education in Chicago last September. "This chapter is devoted to the correlation of the chemical and atomic properties of the transactinium elements with respect to their electronic structure and their place in the periodic table." The concept of a new group of "rare earth" elements, beginning with thorium, emerges with great clarity. No mention is made in this book of elements 99 and 100, recently synthesized by "neutron fattening," but these add still further evidence of the validity of the concept of the actinide series.

An abridged list of topics taken from chapter headings is the easiest way to reveal the scope of this thick book: chemistry of actinium; nuclear properties and chemistry of thorium, protactinium, and uranium; nuclear properties, oxidation states, oxidation-reduction reactions, preparation, and properties of compounds of plutonium; nuclear properties and chemistry of neptunium; nuclear properties and chemistry of transplutonium elements (americium, curium, berkelium, and californium); radiochemical separation of the actinide elements; radiochemical assay by alpha and fission measurement; correlation of properties as actinide transition series; crystal chemistry of the *5f* elements; optical properties of some compounds of uranium, plutonium, and related elements; and finally, slow-neutron and spontaneous-fission properties of heavy nuclei.

Chapter 15 on "Radiochemical separations of the actinide elements," by E. K. Hyde, reviews "the chemical methods which have been developed for the radiochemical isolation and purification of elements of atomic number 89 or higher. The emphasis is largely on the laboratory-scale techniques and methods useful in the isolation of trace amounts of the heavy-element nuclides produced in targets bombarded with the particle beams of a cyclotron or irradiated with neutrons in a nuclear reactor.... It is hoped that the review will be of value to the radiochemist working on any problem requiring for its solution the separation of small amounts of the heavy elements from each other or from the lighter elements...."

Among the volumes of the notable NNES collection of books on the Plutonium Project, this book will be one of the most rewarding for chemistry seniors or graduate students who wish a thorough review of modern inorganic chemistry in an area that constitutes one of the outstanding landmarks in the history of science.

LAURENCE S. FOSTER

BELMONT, MASSACHUSETTS

● ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY. VOLUME XI: POLYOLS TO RUTIN

Edited by *Raymond E. Kirk* and *Donald F. Othmer*, Professors and Heads, Departments of Chemistry and Chemical Engineering, respectively, Polytechnic Institute of Brooklyn. Assistant Editors, *Janet D. Scott* and *Anthony Standen*. The Interscience Encyclopedia, Inc., New York, 1953. xvi + 950 pp. Illustrated. 19 × 27 cm. Single copy price, $30. Subscription price, $28.

As E. C. T. moves toward the concluding volume it is noticeable that the subject treatment is becoming somewhat briefer. Subjects that would have been treated at length in the "C" volumes now are presented concisely, but adequately. The present volume carries a large number of subjects in the various fields of chemistry and chemical technology.

The chemical industries score heavily in this volume with lengthy treatment of power generation, pressure technique, printing and reproducing, pulp, the rayons, refractories, natural resins (synthetic resins are under plastics), resins containing halogen (Teflon and Kel-F), and natural and synthetic rubbers. Shorter treatment is given pressure measurement, printing inks, protein fibers and plastics, refrigeration, rosins and derivatives, and rubber chemicals and compounding.

A new trend in chemical industries is the up-to-date treatment of pyrotechnics and rocket propellants. "Reppe chemistry" is defined as reactions of acetylene under pressure and many examples are given of new reactions and processes.

To assure that industry is making a satisfactory product, a section on quality control is included. This section is broad in scope, including process control, sampling, experimental design, and organization for a quality control program.

The organic chemist finds a considerable number of interesting topics: polysaccharides, propyl alcohols, propyl compounds, propylene, pyridine and derivatives, the quinolines, quinones, free radicals, resorcinol, and riboflavin.

The inorganic chemist scores heavily in this volume with potassium compounds, quaternary ammonium compounds, radioactive elements, radiochemistry, rare earth metals, rhenium and its compounds, and rubidium compounds.

The physical chemist finds somewhat fewer, but important topics: potentiometry, Raman effect, reaction kinetics, refractometry, and rheology.

The year 1954 should conclude E. C. T. All are looking forward to the completion of the set, and to the announcement of plans for revisions and expansions to keep E. C. T. up to date.

KENNETH A. KOBE

UNIVERSITY OF TEXAS
AUSTIN, TEXAS

● TRATADO DE QUÍMICA ORGÁNICA. SIX VOLUMES

***Enrique V. Zappi*, Professor of Organic Chemistry, The University of Buenos Aires. Second edition. Librería "El Ateneo" Editoriál, Buenos Aires, 1952. 3900 pp. 16 × 24 cm.**

THIS extensive text of organic chemistry is a collection and amplification of lectures given by the author at the University of Buenos Aires, Argentina. Organic chemistry is presented through a

classical, descriptive approach but enough electronic theory has been introduced to make the book a modern text. The text has been written for a student beginning his training in organic chemistry. There is, however, sufficient material included for a more advanced student. The book is also useful as a reference work because of a well compiled index.

The style reflects somewhat the atmosphere of the lecture room and makes easy, though productive, reading. Short biographical sketches in the form of footnotes on some of the past and present contributors to the field of organic chemistry and chemical theory add to an already interesting presentation.

The first part (in three volumes) deals with the aliphatic compounds. The systematic discussion of the hydrocarbons and their derivatives is preceded by eight chapters covering such topics as purification of organic compounds, qualitative and quantitative organic analysis, determination of physical constants, and general theory pertinent to organic chemistry. The next 27 chapters describe the chemistry of aliphatic compounds. Emphasis in the discussion is placed on methods of preparation, reactions, and properties of compounds, as well as occurrence. Last but not least, the industrial and commercial importance of the compound is stressed. The final chapter of Part I is devoted to cyclic ureids and purine derivatives.

The second part, also in three volumes, is devoted to cyclic compounds. The first chapter treats very ably the structure of benzene and the problems connected with its elucidation. The chemistry of aromatic compounds is discussed in the following 18 chapters. The pattern of presentation follows that established in Part I. Special emphasis is placed on technically important compounds, with three chapters being devoted to dyes derived from coal tar.

Cyclic compounds are presented in the next six chapters, of which two deal with biologically important material such as vitamins, hormones, and naturally occurring pigments.

The final six chapters of the text deal with heterocyclic compounds. The presentation centers again around technically significant materials and fundamentals are introduced only to the degree necessary for the proper understanding of such classes of substances as pharmaceuticals and alkaloids.

Numerous synoptic tables containing physical constants as well as the Beilstein references of the compounds discussed are useful for quick reference. The graphical presentation of the book is good, although the numbering of the pages should have been done more carefully. The clarity of some line drawings could be improved by increasing their scale. Unfortunately, a few cross references are in error, obviously retaining the page number of the first edition.

HANS A. SUTER

Rollins College
Winter Park, Florida

● CHEMISTRY OF THE LANTHANONS

R. C. Vickery, Division of Industrial Chemistry, C.S.I.R.O., Melbourne, Australia. Butterworths Scientific Publications, London; Academic Press, Inc., New York, 1953. viii + 296 pp. Figs. 32 tables. 14 × 22.5 cm. $6.

The tremendous increase in interest in the chemistry of the lanthanons—the rare earth elements of tradition—which has characterized the past several years has made very apparent the need for a modern and comprehensive treatise in this field. In compiling the present volume, Dr. Vickery has helped to fill in this void, but unfortunately there is still a relatively large volume of information that requires collection and systematic treatment.

The "Chemistry of the Lanthanons" is primarily descriptive in character, with major emphasis being placed upon techniques of separations. As such, it is quite generally adequate, although it does tend to overempbasize the importance of some contributions to the exclusion of others. Both older and more modern techniques are discussed, and from them the author, drawing heavily upon his own experience, derives a general scheme which embodies the best features of both. Unfortunately, the ion-exchange technique is given much less coverage than its importance dictates, and the unfavorable impression given of solvent extraction procedures must be refuted by the remarkable advances made in this field since the manuscript was prepared. The treatment given is unique, however, in its emphasis upon the extreme care necessary for complete and ultimate purifications.

The volume is regrettably deficient in theoretical treatments, and where theoretical concepts are discussed, full advantage of their potentialities is not taken. This is particularly true, for example, in Chapter 3 on Structure, Spectroscopy, and Paramagnetism, which is often confusingly written and quite generally superficial. This is, in the opinion of the reviewer, most unfortunate, because so much that is seemingly unusual in the chemistry of the lanthanons and so many of the regularities apparent among them are so elegantly described by applications of the theoretical and semitheoretical concepts of electronic configurations.

Unfortunately, too, there are many mistakes both in context and in printing scattered throughout the book. The names of authors have seemingly suffered particularly in this respect, and a number of apparently careless omissions of credit have been made. The style is all too often circuitous and the presentation obtuse. A fascinating subject is thus made to appear unnecessarily dull.

In spite of its obvious deficiencies, the book contains much that is good and interesting and should aid in focusing increased attention upon this group of elements. It is to be hoped that the author will make necessary improvements in an early revision.

THERALD MOELLER

University of Illinois
Urbana, Illinois

● NUCLEAR MOMENTS

Norman F. Ramsey, Harvard University. John Wiley & Sons, Inc., New York, 1953. x + 169 pp. 38 figs. 4 tables. 15 × 23 cm. $5.

The increasing variety of applications of nuclear magnetism to chemical problems is rapidly developing a need for a comprehensive book in the field. It is unfortunate, at least for the chemist, that Professor Ramsey's book is a less ambitious undertaking.

The first four chapters were written in early 1952 and published as Part III, "Nuclear moments and statistics," in Volume I of "Experimental Nuclear Physics" (John Wiley & Sons, Inc., New York, 1953), edited by E. Segrè. These chapters are concerned with the aspects of the subject which are of predominant interest to nuclear physicists. A fifth chapter on applications to chemistry and solid-state physics was written in the spring of 1953. This chapter is combined with the earlier work to form the present volume. The origins of the book suggest its usefulness and also its limitations.

In the first two chapters the author describes the characteristics of nuclear moments and summarizes the theory of interactions between nuclear moments and electric and magnetic fields. The experimental methods used in measuring nuclear moments and the various interactions are given in the next chapter. Professor Ramsey's extensive research on molecular and atomic beams finds expression in a particularly lucid summary of the art. The fourth chapter gives a complete tabulation of nuclear moment data and includes a brief account of the implications of the results in nuclear structure.

The last chapter, on the rapidly growing applications to other structural problems, is the part of most interest to chemists. However, it is in the nature of a survey, with relatively few details, and the discussion lacks integration with the first section of the book. The reader who is new to the field is impressed by

the diversity of results, but he needs much more background before considering applications to his own problems. However, an excellent and complete bibliography is given, as well as key references to the original literature.

A book on a highly active new field of research may be comprehensive one year but sadly incomplete the next. And this would be the case for any book at this time on nuclear magnetism, even if it were thrice as long as Ramsey's book. Nonetheless, there is a real demand for reports on the utility and development of the field. And the author and publishers have performed a very useful service in making available a current, though inevitably limited, review.

H. S. GUTOWSKY

UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

● DICTIONARY OF ORGANIC COMPOUNDS. 4 VOLUMES

Sir Ian Heilbron **and** ***H. M. Bunbury,*** **Editors-in-Chief. Second edition. Oxford University Press, New York, 1953. Vol. I, xvi + 654 pp.; Vol. II, xvi + 845 pp.; Vol. III, xvi + 838 pp.; Vol. IV, xvi + 694 pp. 19 × 26 cm. $78 per set.**

THE publication of this new edition of "Heilbron" fulfills the hope of many chemists and the promise of the editors that this useful reference work would be kept reasonably up to date. At the time that the first edition appeared in 1934–37, it was the intention to make a complete revision every five or six years. This plan was prevented by the war, although a revised edition of Volume I appeared in 1943 and Volumes II and III were reprinted with supplements in 1944. According to the preface, the whole of the text of this new edition has been examined carefully and revised in the light of publications through 1950, and some material is as recent as the early months of 1953. The size of the new edition has been increased by 2500 entries and 535 pages. To facilitate handling, the revision consists of four volumes instead of three. Such expansions are useful but cannot be continued indefinitely without sacrificing the advantages of a convenient handbook. In the present instance, the increased amount of material has been accommodated by increasing the printing area by 30 sq. cm. per page and by using a thinner paper. One of the most remarkable accomplishments of the publishers is the establishment of a price for the four-volume set in 1954 at only three dollars more than for the three-volume set in 1934.

The type of information included remains the same as in the first edition. The formula of the compound is followed by the source if a natural product, the physical properties, derivatives and their physical properties, and references to methods of preparation and constitution.

As an example of the changes that have been made, the first page of the first edition has entries for Abietic Acid, Absinthin, Acacetin, Aceanthrenequinone, and Acenaphthaquinoline. In the new edition Acenaphthaquinoline appears three-fourths of the way through page 2, the entries up to this point being Abadole, Abienol, Abietic Acid, Abietinol, Abrine, Acacetin, Acaciabiuronic Acid, Acaciin, Aceanthrene, and Aceanthrenequinone, with cross references forAceconitic Acid, Acenaphthanthracene, Acenaphthapyridine, and Acenaphthaquinoline.

The three entries appearing in the first edition have been expanded even when no new references are cited. As may be expected in a work of this sort, the material presented is not all that one would like it to be. For example, under Abietic Acid the statement, "Forms an additive compound with maleic anhydride," hardly conveys the fact that the reaction involves rearrangement and that the adduct is that of sapietic acid and not abietic acid. Somewhat higher values for the melting point and rotation than those given have been recorded, and the ultraviolet absorption maximum has been found to be at 241 mμ rather than 237.5 mμ. Although nine references to the original literature are given, that to the work of Harris in 1948, which showed that abietic acid is a natural constituent of the oleoresins and not merely a rearranged product, is missing. Also one might have expected a reference to the useful review on the chemistry of the resin acids published by Zeiss in 1948. Although papers by Harris and Sanderson are cited under pimaric and sapietic acids, there is no entry for neoabietic acid nor for isodextropimaric acid reported in the same articles. The latter omission is all the more surprising since isodextropimarinal, isolated in later work by Harris and Sanderson, is listed. Of course it is purely accidental that the reviewer happened to be familiar with the chemistry of a compound listed on the first page of the first volume, and it is not intended to imply that these adverse comments are representative of the volume as a whole. On the other hand it does emphasize the fact that no handbook can be depended upon to take the place of a careful literature search.

Two general objections may be made to the "Dictionary" which could have been improved in the new edition. When one is confronted with eight or ten references to the original literature, it would be helpful to have some indication of their content other than the statement in the preface that they relate to methods of preparation or determination of constitution. The other general objection is that not only is no uniform system of nomenclature adopted, but where a systematic procedure is used for indexing purposes, it does not follow any of the more familiar systems. Since by far the largest number of entries is by common names or their simple derivatives, this difficulty is not as great as one might expect. However, anyone attempting to use the dictionary should read the introduction, which is repeated in each volume.

As a handy reference book to organic compounds and a guide to recent literature, the "Dictionary" remains a very useful tool for all chemists.

CARL R. NOLLER

STANFORD UNIVERSITY
STANFORD, CALIFORNIA

● A FRENCH-ENGLISH DICTIONARY FOR CHEMISTS

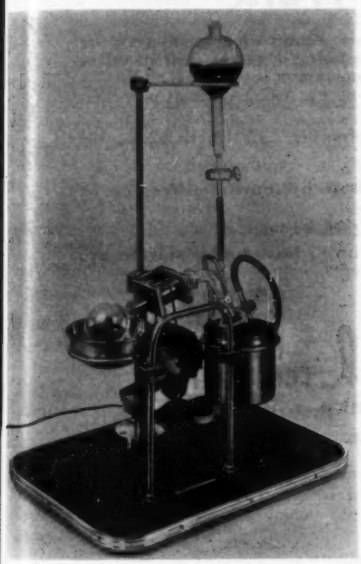
Austin M. Patterson, **Professor Emeritus of Chemistry, Antioch College. Second edition. John Wiley & Sons, Inc., New York, 1954. xiv + 476 pp. 13.5 × 18.5 cm. $6.50.**

THIS is a new and enlarged edition of a dictionary first published in 1921, and it now contains about 42,000 terms.

Out of the Editor's Basket

Automatic Distilling Apparatus

E. Machlett & Son has just introduced a new, automatic distilling apparatus—Rotovap—designed for the safe, rapid, efficient, and convenient evaporation of solutions, either diluted or concentrated,



by batch or continuous operation. It is claimed that Rotovap literally revolutionizes laboratory distillation procedures.

According to Machlett, once the apparatus is set in motion it will automatically distill 100 ml. of aqueous solution at 55 degrees Centigrade in 10 to 15 minutes under the reduced pressure of an ordinary water aspirator. Furthermore, Machlett says, Rotovap is equally effective for the distillation of non-aqueous, high-boiling solutions such as butanol.

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Separatory Funnel Eliminates Lubrication and Freezing Problems

A new glass separatory funnel developed by Fischer & Porter Co. eliminates stopcock lubrication and freezing problems. The Ultramax valve of the separatory funnel consists of a teflon plug which turns on the natural glazed surface of an unground, precisely-formed section of pyrex tubing. The unit is adapted to centrifuging, and product contamination is avoided because valve lubricants are unnecessary.

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Further details of the new separatory funnel are available by writing to the Fischer & Porter Co., 143 Jacksonville Rd., Hatboro, Pennsylvania.

New Panel Type Gas Purity Analyzer-Recorder

The Gow-Mac Instrument Co. announce production of new panel-type instruments for plant stream and laboratory. The new Gow-Mac panel instruments monitor various mixtures and trace impurities. The panels are complete, ready to install in industrial processing systems or laboratory installations. Complete information and literature are available from the manufacturer, Gow-Mac Instrument Co., 100 Kings Rd., Madison, New Jersey.

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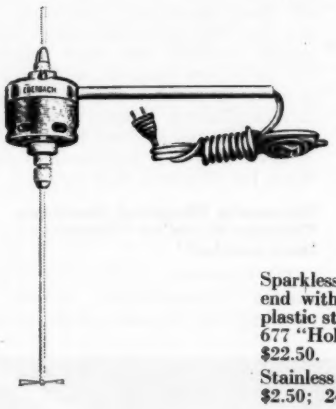

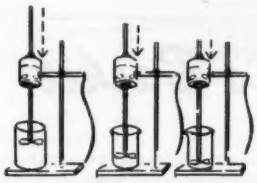

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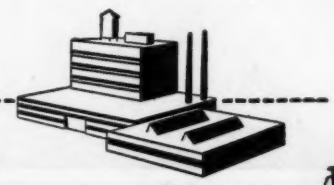

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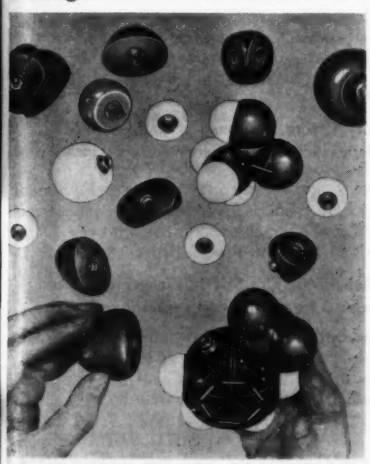
Portable Bunsen-type Burner

A new portable Bunsen-type Burner using LP (Liquefied Petroleum) gas in handy disposable tank, thereby eliminating need for gas piping, is now being introduced by The Turner Brass Works, Sycamore, Illinois. This portability feature—due to the replacement fuel tanks—makes the burner ideal for general laboratory, industrial, and schoolroom use. Unit is $5/8$ in. high in operating position; has all-brass burner, control valve, and fittings; is designed for use with Turner $5/8$ in. Bunsen burner fittings, standard laboratory tripods, hot plates, etc. For complete details, readers are asked to request catalogue sheet No. LP 800.

New Atom Models Attain Magnification of 1.5×10^8

A new set of scaled atom models announced by Arthur S. LaPine Co., advances the magnification of spheres o action of single atoms to 1.5×10^8. The Chicago laboratory equipment firm is sole U. S. A. distributor of these Stuart and Briegleb atom models manufactured by E. Leybold's Nachfolger, Cologne, Germany.

This set of models for studying atomic structure of organic molecules provides the largest variety of structural unit types (28) presently available. Different colors are assigned to the various elements and some are supplied in different types of structural units for various bonds, groups, and rings.



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A free copy of their 8-page, three-color booklet describing and illustrating these atom models is available from Arthur S. LaPine & Co., 6001 S. Knox Ave., Chicago 29, Illinois.

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An improved titration indicator, Methyl-Purple, is now available. It has been cited in the technical literature as a substitute for methyl orange, methyl red, and other indicators for the determination of borax, ammonia in hydrazine, mixed phosphates, nitrogen (Kjeldahl), and alkalinities. It has also been recommended for use in perchloric acid titrations.

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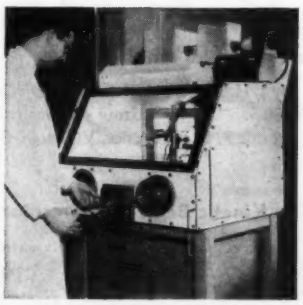

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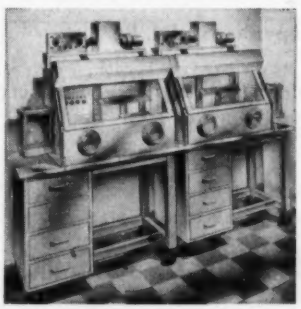

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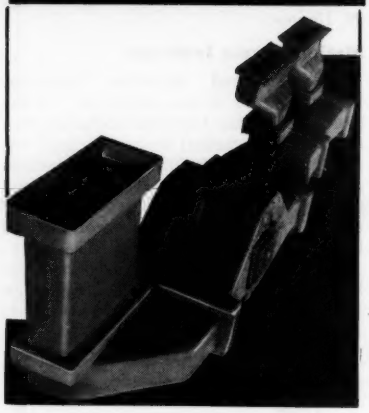

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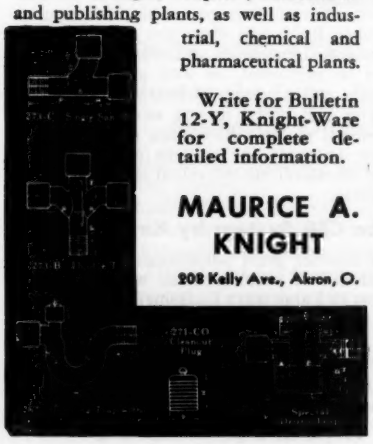

Write for Bulletin 12-Y, Knight-Ware for complete detailed information.

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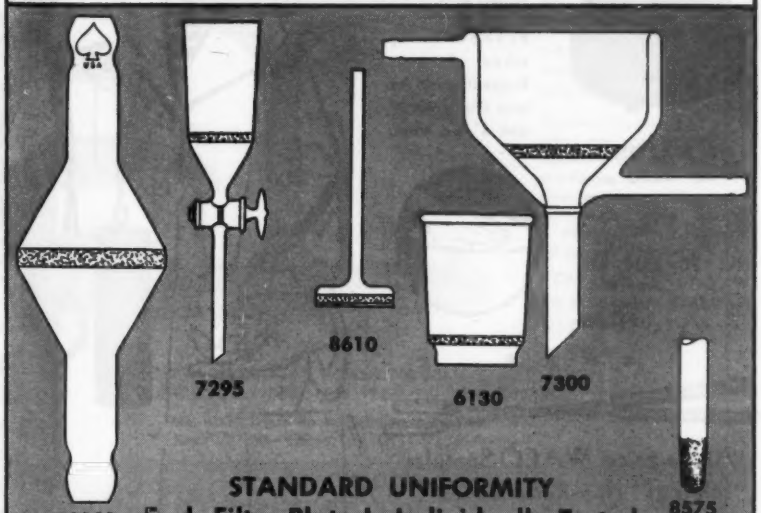

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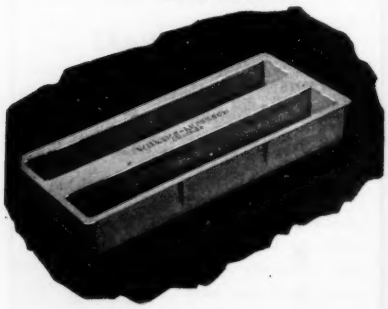

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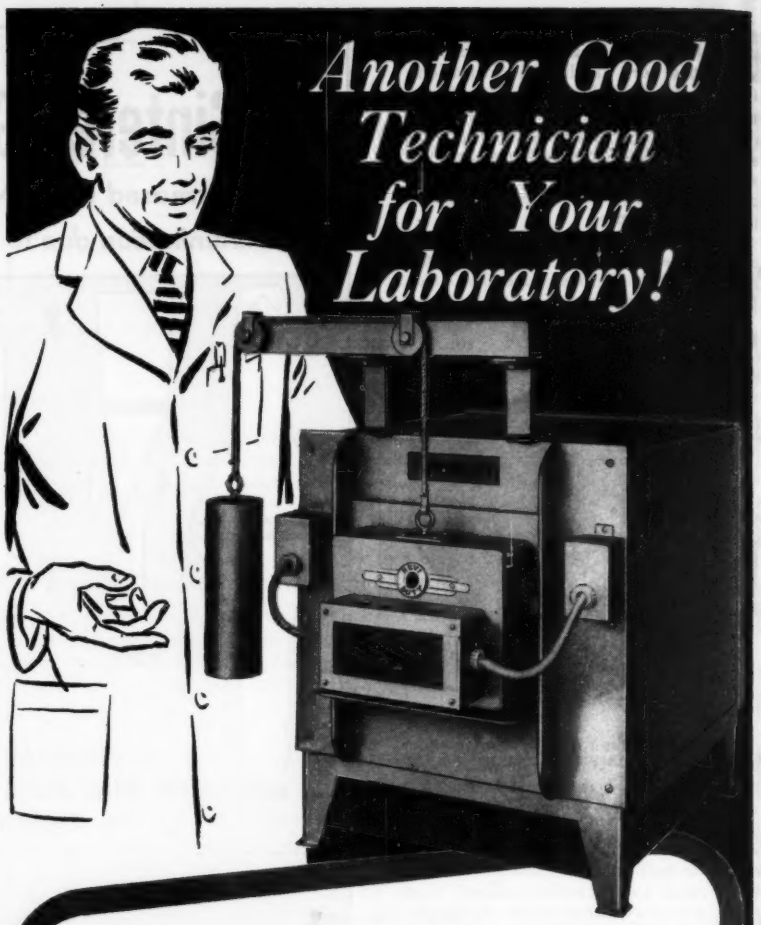

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• Catalogue No. 54-C "Drugs and Chemicals" has just been released by Amend Drug & Chemical Co., 117–119 East 24th St., New York 10, New York. This new catalogue is said to contain the largest listing of organic and inorganic chemicals. Special colored sections are given over to the listing of dyes, culture media, and supplies for pH and chemical control.

Copies of catalogue No. 54-C are available, free, if requested on an official letterhead.

• A bulletin on the new Wurm-Standard paper strip electrophoresis apparatus has just been released by Standard Scientific Supply Corporation, 34 West 4th St., New York 12, New York. The bulletin illustrates the apparatus, describes it in detail, and lists its many advantages. Prices for the apparatus and components are also given. Copies of the bulletin are available on request.

• Coleman Instruments is issuing a new 64-page catalogue. In addition to a complete listing of Coleman instruments and accessories, the book contains brief descriptions of the most widely used analytical systems. Included are complete discussions of theory and practice of Absorption Spectrochemistry, Nephelometry, Colorimetry, pH measurement, Fluorimetry and Flame Photometry. Copies are available without charge if requested on company letterhead. Write to Coleman Instruments, Inc., 318 Madison St., Maywood, Illinois.

• A new 8-page, two-color brochure completely describing the new Model 38-A Tiselius Electrophoresis Apparatus has just been published by The Perkin-Elmer Corp. Featured in the brochure is a section on the use of electrophoresis in modern analytical techniques, and specifications and descriptions of the components of the Model 38-A. Included among the latter are descriptions of the new Land camera that makes finished pattern prints in 60 seconds, a powerful light source 15 times the intensity of the old, and a ground glass screen for observation of the patterns during the critical

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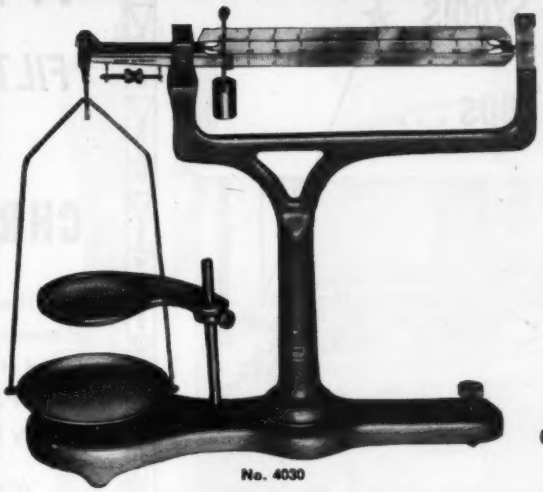

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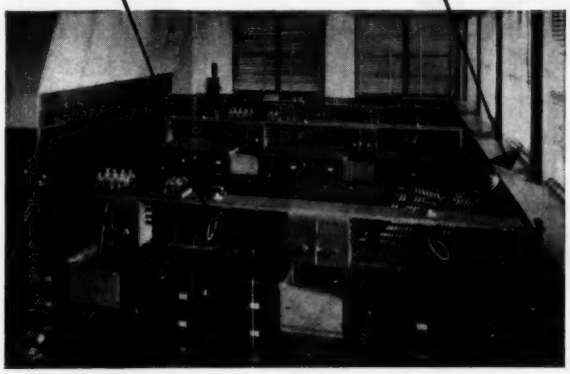

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● The Nuclear Instrument and Chemical Corp., 229 West Erie St., Chicago 10, Illinois, has recently printed a new 40-page, two-color catalogue describing its complete line of radiation-measuring equipment including scalers, count rate meters, Geiger, proportional and scintillation counters, complete radioisotope laboratories, etc. Copies will be sent on request.

● Schaar and Company offers a new catalogue illustrating and describing their extensive line of ovens for the laboratory and plant. Laboratory models include all-Stainless Steel Gravity Convection ovens, Forced Draft ovens, High Temperature ovens, and Mechanical Convection ovens which for the first time solve the variable air-weight problem. For plant use, larger, batch-type units are described. All models incorporate many design and operational improvements presented for the first time. Available on request from Schaar and Company, 754 West Lexington St., Chicago 7, Illinois.

● New LaPine chemical catalogue lists prices of laboratory and industrial chemicals in quantities from ounces to hundreds of pounds from cc.'s to multiple-gallon drums. After the 32-page alphabetical listing of technical chemicals and laboratory reagents are sections on diagnostic and histological reagents, staining solutions, dry biological stains, reagent solutions, pH indicators (dry or in solution), aniline and coal tar dyes, certified colors for foods, drugs and cosmetics, dehydrated culture media products, bacto-sensitivity discs, prepared culture media, serological reagents and vitamins. For copy of chemical catalogue, write to Arthur S. LaPine & Co., 6001 S. Knox Ave., Chicago 29, Illinois.

● A new, complete, factual 245-page reference catalogue is now available from the J. T. Baker Chemical Co. This special Golden Anniversary catalogue lists the entire line of "Baker Analyzed" Reagents and shows the latest specifications. This new catalogue lists 5 new primary standards, 62 new chemicals, and 600 improvements in specifications. It is a real time-saver for users and buyers of laboratory chemicals who want prices and latest specifications quickly available. A free copy of the Baker Golden Anniversary catalogue will be sent upon request. For your catalogue, address: J. T. Baker Chemical Co., Reagent Chemical Division, Phillipsburg, New Jersey.

● A description of Koppers Styrene Monomer and its uses is contained in a 24-page bulletin issued by the Chemical Division of Koppers Co., Inc. Products obtained from this basic chemical, and their applications, as listed in this new illustrated bulletin, include synthetic rubber, polystyrene, styrene butadiene latices, polyester resins, styrenated drying oils, styrenated alkyds, ion-exchange resins, styrene-acrylonitrile copolymers, sty-

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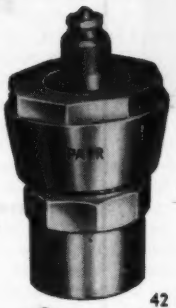

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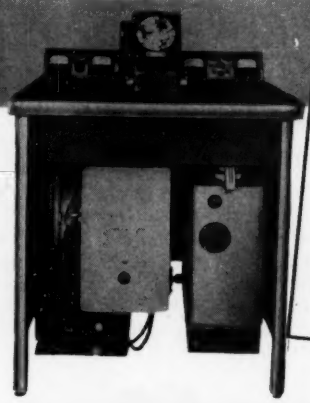

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References

(1) Ind. Eng. Chem. 25-653 (June, 1933)

(2) Ind. Eng. Chem. 25-1112 (Oct., 1933)

(3) National Bureau of Standards Journal of Research 12-241 (Feb. 1934, R.P. No. 649)

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ne-maleic resins, and other chemical erivatives. Properties of the derivatives nd specifications of Styrene Monomer are lso given. Copies of this publication may e obtained by addressing a request for ulletin C-4-198 to Koppers Co., Inc., hemical Division, Koppers Building, ittsburgh 19, Pennsylvania.

"Scientific Apparatus & Methods," olume Six, No. 2, is now available from . H. Sargent & Co., 4647 W. Foster Ave., hicago 30, Illinois. This issue features an rticle on their centrifugal wet mill for nalytical sample reduction. The article escribes the design, operation, procedure, nd applications of the mill.

More than a dozen important water reatment processes are serving industry oday. To explain these variations, how hey work, the equipment they require nd the type of water they produce, Rohm & Haas Company has compiled a 4-page booklet entitled "If You Use Water."

Illustrated liberally with two-color low diagrams, the booklet discusses the undamentals of the three major classifica-ions of industrial water treatment based n ion exchange: softening, dealkaliza-ion, and deionization. Under each of hese classifications, the booklet presents he major process variations.

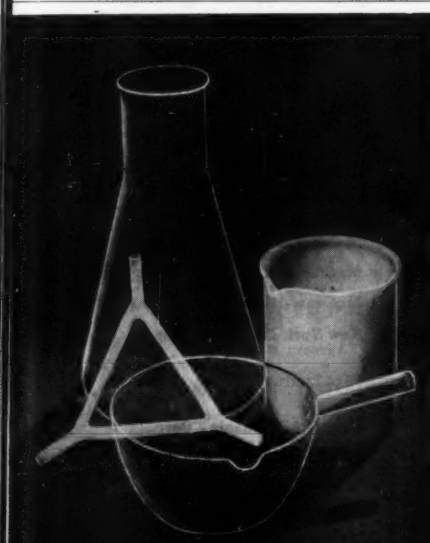
For example, the deionization section escribes multiple and mixed bed systems nd why different types of water supplies equire different *combinations* of ion ex-hange resins and equipment to produce ffluent water of a given quality.

The advantages of the various water treatment methods are discussed and interpreted in terms of the applications in specific industries. Copies of the booklet may be obtained on request to Rohm & Hass Co., Resinous Products Division, Washington Square, Philadelphia 5, Pa.

● A new booklet, "Organic Acids," has just been published by Carbide and Carbon Chemicals Company, a Division of Union Carbide and Carbon Corporation. This booklet discusses in detail the eight organic acids that are sold in commercial quantities by the Company (acetic, butyric, 2-ethylbutyric, caproic, 2-ethylhexoic, crotonic, sorbic, and succinic acids). It tells of their uses in many industries, and gives their physical properties, specifications, shipping data, and constant boiling mixtures. The sections on physical properties and specifications will be helpful in suggesting uses, and in determining proper handling and storage procedures. Selected references are included.

An important feature of this booklet is an entire section devoted to the specifications and test methods used by Carbide for its organic acids. These laboratory control tests comprise some of the standard A.S.T.M. methods, as well as new methods that have been specially developed by the Company's own laboratories. The reader will, therefore, be able to use the booklet as a guide in his analytical laboratory when working with these organic acids.

Copies of this new booklet, "Organic Acids" (F-4768) are available from Carbide and Carbon Chemicals Co., 30 East 42nd St., New York 17, New York.



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Agency: *Ray Hawley*
Ainsworth & Sons, Inc., Wm. 11
Agency: *Walter L. Schump, Adv.*
Alberene Stone Corp. of Va. 28
Agency: *G. M. Basford Co.*
Amend Drug & Chemical Co., Inc. 34
American Optical Co. 33
Agency: *Baldwin, Bowers, & Strachan, Inc.*
Angel & Co., Inc., H. Reeve 28

Baker Chemical Co., J. T. ..... IFC
Agency: *Wildrick & Miller, Inc.*
Beckman Instruments, Inc. 12
Agency: *Darwin H. Clark Co.*
Blakiston Co., The 13
Agency: *L. W. Frohlich & Co.*

Chem Ed Buyers' Guide 32
Coleman Instruments ..... FC
Agency: *Jack Hollander*
Coors Porcelain Co. 34

Daigger & Co., A. ..... IBC
Agency: *R. I. David & Co.*
Delta Chemical Works, Inc. 30
Agency: *Miller Adv. Agency, Inc.*

Eaton-Dikeman Co. 27
Agency: *Olian-Sidman Adv. Agency, Inc.*
Eberbach Corp. 22
Agency: *Thomas F. Lacy, Adv.*

Farrand Optical Co., Inc. 30
Agency: *Firestone Adv. Agency, Inc.*
Fisher Scientific Co. ..... BC
Agency: *Smith, Taylor & Jenkins, Inc.*

Greiner Co., Emil 8
Agency: *Fairfax, Inc.*

Hammond Drierite Co., W. A. 30
Hevi Duty Electric Co. 26
Agency: *Camm, Costigan & Seitz, Inc.*

Kewaunee Mfg. Co. 23
Agency: *Rogers & Smith*
Klett Mfg. Co. 20
Knight, Maurice A. 2
Agency: *Brown Advertising Agency*

Laboratory Furniture Co. 2
Agency: *Dundes & Frank, Inc.*
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Agency: *Atherton & Currier, Inc.*
Mallinckrodt Chemical Works 9
Agency: *Smith & Williams Adv., Inc.*
Matheson, Coleman & Bell, Inc. 1
Agency: *Firestone Adv. Agency, Inc.*
McGraw-Hill Book Co., Inc. 6

New York Laboratory Supply Co., Inc. 2
Agency: *Raf Adv., Inc.*

Parr Instrument Co. 2
Agency: *F. Willard Hills Adv. Service*

Reinhold Publishing Corp. 4
Agency: *Waterston & Fried, Inc.*

Sargent & Co., E. H. 1
Agency: *Kreicker & Meloan, Inc.*
Schleicher & Schuell Co., Carl 3
Agency: *Wildrick & Miller, Inc.*
Scientific Glass Apparatus Co., Inc. 1
Standard Scientific Supply Corp. 7
Agency: *Firestone Adv. Agency, Inc.*

Thermal Syndicate, Ltd. 3
Agency: *Asher, Godfrey & Franklin, Inc.*
Thomas Co., Arthur H. 3

U. S. Stoneware Co. 2
Agency: *Ralph Gross Adv., Inc.*

Welch Scientific Co., W. M. ..... 18 & 2
Agency: *H. A. Hooker Adv. Agency, Inc.*
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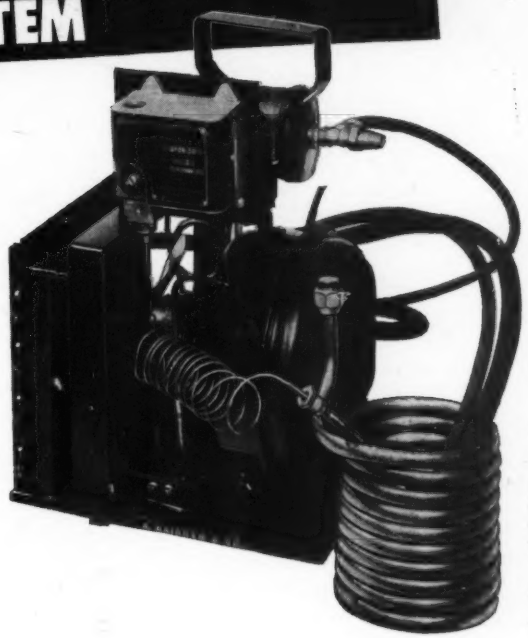

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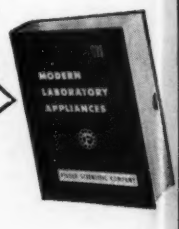
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